ORGANOPLATINUM COMPLEXES OF CYCLIC ALLENES, ALKYNES AND CARBENES: SYNTHESIS, STRUCTURE AND PROPERTIES

BY

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TO MY WIFE MANQIAN AND SON XINGXING

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This work would have not been possible without my research advisor, Professor William M. Jones. His guidance, patience, and encouragement helped to sustain me during those periods of frustration; his intelligence and modesty often reminded me to be prudent, cautious, and modest when things went well. It truly has been a pleasure to work for him and learn from him. Those happy moments will live with me forever. Thanks are also due to Dr. Roy W. King for teaching me those advanced NMR technologies; to Dr. Khalil Abboud for performing the X-ray crystal studies for me; and to Linda Cannon, Rhonda Trace, and many other people for improving my English and teaching me about American culture.

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

ORGANOPLATINUM COMPLEXES OF CYCLIC ALLENES, ALKYNES AND CARBENES: SYNTHESIS, STRUCTURE AND PROPERTIES

By

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August, 1992

Chairman: Dr. W. M. Jones
Major Department: Chemistry

The first tropyne (a tropylium ion analogue of benzyne) bistriphenylphosphine platinum complex 1-15 and the first (*trans*-bromobistriphenylphosphine)(cycloheptatrienylidene) platinum complex 1-12 were prepared. Their structures were characterized by standard identification methods (NMR, IR, etc.). The NMR data of these two complexes are discussed in terms of σ-bonding and π-back bonding interaction between the metal fragments and the tropylium ion ligand. The successful preparation of 1-12 also provides more evidence to support the suggestion that the seven-membered ring form of C_7H_6 prefers a cycloheptatetraene (allene) form to a cycloheptatrienylidene (carbene) form if it is complexed to a high-electron-density metal fragment, e.g., Pt(0), which has ten d electrons. This preference, however, will be reversed

if C_7H_6 is complexed to a low electron density metal such as Pt(II) which has eight d electrons.

The proton NMR spectrum of (1,2-η^2-cycloheptatetraene)-bistriphenylphosphineplatinum 1-9 was characterized by NMR COSY, NOE and deuterium labeling. From an X-ray crystal structural study of 1-9, it was found that the dihedral angle between H3 and H2 in 1-9 is nearly 90°. This result explains why there is no coupling between H3 and H2, a fact which had caused the COSY spectrum to be misleading.

The fluxional process of 1-9 was studied by NMR spin saturation transfer and NOESY. The activation parameters were determined: $\Delta H^{\neq}$=26.8 Kcal/mole, $\Delta S^{\neq}$=15.1 eu. The mechanism of the fluxional process was found to be intermolecular. The fluxional process of (1,2-η^2-cycloheptadiene)bistriphenyl-phosphine platinum 5-1 was found to be significantly slower than that of 1-9.

The mechanisms of the formation of 5-1 and 1-9 were investigated. The possibility of the so-called insertion mechanism was excluded, but both a trapping mechanism and a π-complex mechanism remain viable possibilities.

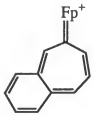
Finally, lithium diisopropylamide (LDA) was discovered to be a good base for removing HBr from a double bond in cyclic alkene compounds and for producing cyclic alkyne complexes of bistriphenylphosphineplatinum. Using this base, complexes of cycloheptyne, cyclohexyne, cyclohepta-3,5-dien-1-yne and cyclohepta-3,6-dien-1-yne were successfully prepared.

CHAPTER 1
INTRODUCTION

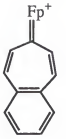
An important aspect of organometallic chemistry has been the stabilization of organic reactive intermediates by coordinating them to transition metal fragments.[1] Molecules possessing carbene,[2-4] strained double bonds[5-8] and strained triple bonds[9-13] complexed to transition-metal centers have been successfully prepared. Not only do they show remarkably different chemistry from the parent hydrocarbons, but many also show catalytic and stoichiometric activity in organic synthesis.[14-17] A clear understanding of such complexes is therefore of fundamental importance in that it may help us develop new synthetic reagents and better understand catalysis.

Recent research in our laboratory has focused on transition metal complexes of reactive intermediates and strained, closed-shell molecules derived from cycloheptatriene and its benzannelated derivatives. These include the successful preparation of the cyclocarbene complexes of Fe(II) 1-1, its benzannelated derivatives 1-2 and 1-3;[18] Ru(II) 1-4, its benzannelated derivatives 1-5, 1-6 and 1-7;[19] and W(0) 1-8.[20] These also include the successful preparation of cycloallene complexes of Pt(0) 1-9, 1-10, and 1-11.[21]

1-1



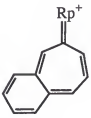
1-2



1-3

Fp= $(\eta^5\text{-}C_5H_5)Fe(CO)_2$

1-4



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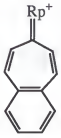
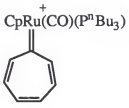


1-6

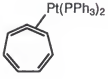
Rp= $(\eta^5\text{-}C_5H_5)Ru(CO)_2$



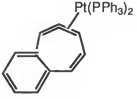
1-7

1-8

Cp=$\eta^5\text{-}C_5H_5$



1-9



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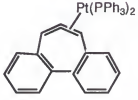
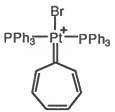


1-11

These results clearly show that transition metal complexes of the seven-membered ring, C_7H_6, (derived from cycloheptatriene) and its benzannelated derivatives can exist in the carbene form or in the allene form as their ground states. The preference for carbene or allene varies with the metal to which the C_7H_6 is coordinated.

In this dissertation, research in the area of reactive intermediates and strained closed shell molecules derived from cycloheptatriene is expanded to include: 1) a detailed experimental study of fluxionality in 1-9 and experiments designed to address the mechanism of its formation; 2) preparation of the first Pt(II) carbene complex of C_7H_6 1-12 and a comparison of its structure with that 1-1, 1-4, 1-7 and 1-8; 3) preparation of the first recorded platinum complexes of two isomeric cycloheptadienynes 1-13 and 1-14; and 4) preparation of the first example of a transition metal complex of the cycloheptadienyneylium ion (called tropyne) 1-15 and a detailed study of its structure, bonding and physical properties.



1-12

1-13

1-14

1-15

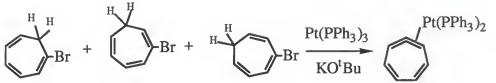
CHAPTER 2

PREPARATION AND STRUCTURAL ANALYSIS OF (1, 2-η^2-CYCLOHEPTATETRAENE)BIS(TRIPHENYLPHOSPHINE)PLATINUM

Introduction

Our initial purpose was to study the fluxional process of complex 1-9. In order to do this, a fully characterized sample was required. Complex 1-9 had previously been synthesized by Winchester by the following reaction (Eq.2-1).[21]

Eq.2-1



2-1 2-2 2-3 1-9

When repeating his work, we found that a slight modification of the procedure significantly reduced side reactions. As a result, we were able to obtain X-ray quality

crystals. Therefore, the X-ray crystal structure of 1-9 was obtained.

Proton NMR Spectrum of 1-9

A ^{1}H NMR spectrum of 1-9 is shown in Fig.2-1. This spectrum is difficult to interpret in terms of assignment of resonances. At first glance, the peaks at 3.41 ppm (one of the satellites down-field is overlapped with THF peak) would be assigned to H2 and the peak at 4.97 ppm would be assigned to H7 because (a) these peaks have a central peak and two satellite peaks on each side, which is characteristic of protons close to a platinum and coupled to the ^{195}Pt isotope; and (b) from the literature,[6,22] in general it appears that the closer a proton is to a platinum, the farther up-field its chemical shift. Proton H2 is two-bonds away from the Pt while H7 is three-bonds away; therefore, H2 should be at 3.41 ppm.

However, when the structure of 1-9 is examined more closely, it is apparent that H3 is also three-bonds away from the Pt atom. Careful examination of Fig.2-1 reveals another peak (at 6.16 ppm) that has a central peak and two satellite peaks too. It therefore became necessary to unequivocally determine which hydrogen, H3 or H7, gives rise to the peak at4.97 ppm and which leads to the peak at 6.16 ppm. This was first attempted using 2D NMR (COSY) and NOE.

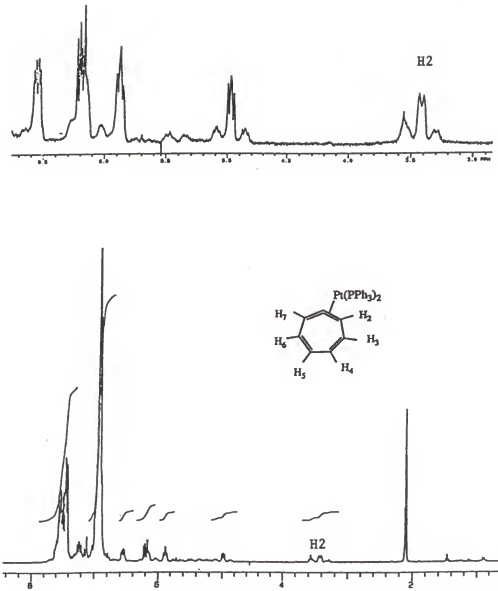


Fig.2-1. The ^1H NMR spectrum of 1-9.

2D NMR(COSY) and NOE Studies of 1-9

Proton 2D COSY (homonuclear chemical shift correlation spectroscopy) NMR is very helpful in determining how protons are coupled to each other. The COSY spectrum of 1-9 is shown in Fig.2-2. There is a crosspeak(spot A) between the peak of H2 and the peak at 6.16 ppm. There is no crosspeak between H2 and the peak at 4.97 ppm. A crosspeak in the COSY spectrum represents a J-coupling between two protons. Proton H2 is three-bonds away from H3 and four-bonds away from H7. Therefore, H2 would normally be expected to couple more strongly to H3 than to H7. As a result, it would appear reasonable to assign the peak at 4.97 ppm to H7 and the peak at 6.16 ppm to H3.

Proton H2 is also closer in space to H3 than to H7 and should show a larger NOE effect with H3 than with H7. It was therefore surprising that an NOE experiment (Fig.2-3) showed 6% NOE enhancement between H2 and the peak at 4.97 ppm, but no observable NOE enhancement was found between H2 and the peak at 6.16 ppm. These results suggested that the peak at 4.97 ppm should be H3 and the peak at 6.16 ppm should be H7.

These contradictory results from the NOE and COSY experiment forced us to find another method to unequivocally assign the proton resonances in 1-9. For this purpose, a deuterium labeling experiment was designed in which H2 and H7 were specifically replaced with deuterium to determine which peaks disappear in the ^{1}H NMR spectrum.

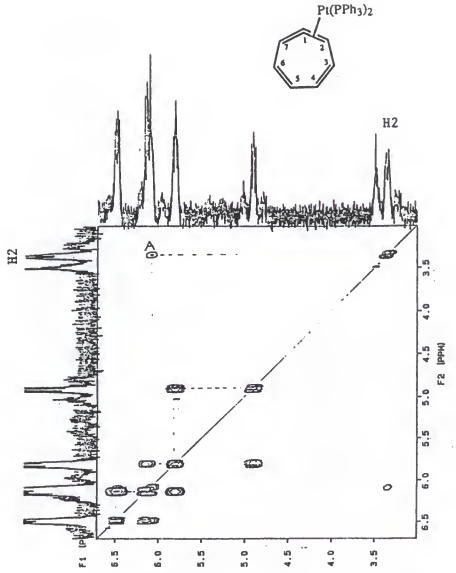


Fig.2-2. The COSY spectrum of 1-9.

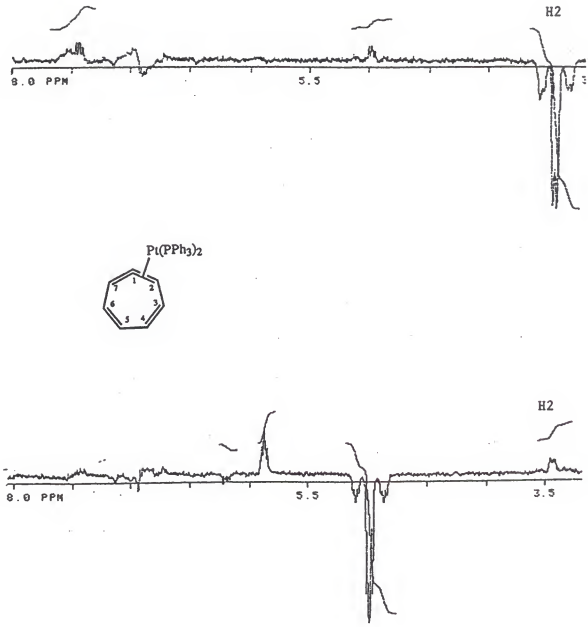


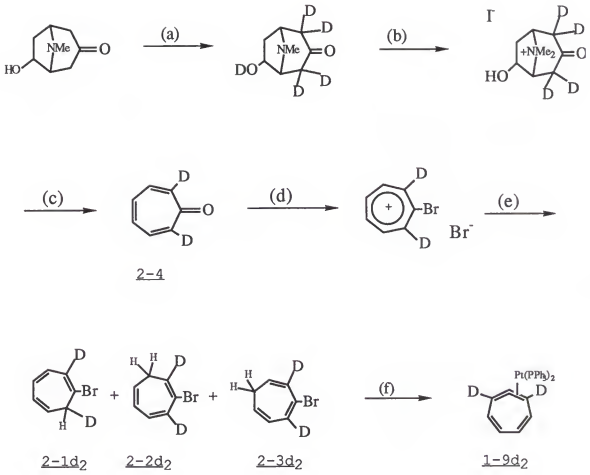
Fig.2-3. The NOE spectrum of 1-9. a) Saturation of the resonance at 3.41ppm; b) Saturation of the resonance at 4.97ppm.

Synthesis of (1, 2-η^2-Cycloheptatetraene-2,7-d_2)-bis(triphenylphosphine)platinum 1-9d_2 and Its NMR Spectrum

Synthesis of 1-9d_2 is summarized in Fig.2-4. Machiguchi et al.[23] have prepared deuterated tropanone 2-4 but they reported no experimental details. Fortunately, the reactions of step (a) and step (c) use D_2O as the reaction solvent. It was therefore possible to monitor the progress of these reactions by ^1H NMR and find appropriate synthetic conditions.

The ^1H NMR spectrum of 1-9d_2 (Fig.2-5) shows no peaks at 3.41 and 6.16 ppm, and the deuterium (^2H) NMR of 1-9d_2 (Fig.2-6) shows two deuterium resonances at 6.16 and 3.14 ppm. (In high resolution deuterium NMR, the resonances are broadened by deuterium quadrupole relaxation more severely for large molecules like 1-9d_2 than for small ones like toluene-d_8.)[24] Therefore, it is clear that the resonance at 6.16 ppm must arise from H7.

Once the chemical shifts of H2 and H7 had been determined based on the crosspeaks in the 2D COSY NMR spectrum (Fig.2-2), the remaining protons could be easily assigned. Thus, H3 is at 4.97 ppm, H4 at 5.87 ppm, H5 at 6.19 ppm and H6 at 6.54 ppm. The complete assignment of all six protons is shown in Fig.2-7. (Without the deuterium labeling experiment and simply with the COSY NMR spectrum Fig.2-2, it was still difficult to assign H7 and H3. If the resonance at 4.97 ppm was assumed to H7, H3 would be the resonance at 6.16 ppm according to Fig.2-2; if the resonance at 4.97 ppm was



(a) K_2CO_3, RT, D_2O, 24 hr; (b) MeI, EtOH, 5 °C, 15hr; (c) $NaCO_3$, D_2O, 60 °C, 10hr; (d) BrOCCOBr, Et_2O, 0 °C; (e) $LiAlH_4$, Et_2O, RT, 2hr; (f) $Pt(PPh_3)_3$, t-BuOK, THF, RT, 8hr.

Fig.2-4. The scheme of the synthesis of 1-9d_2.

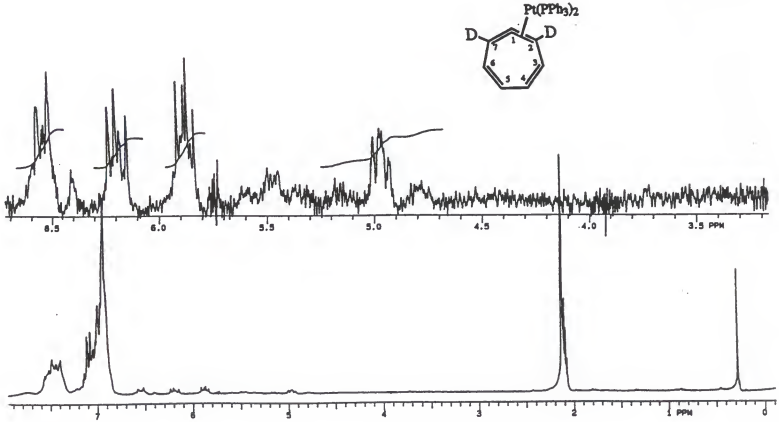


Fig.2-5. The ^1H NMR spectrum of 1-9d_2.

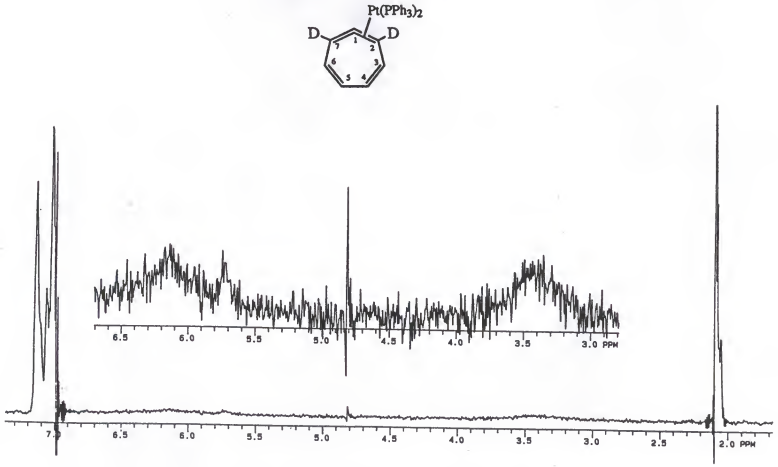


Fig.2-6. The deuterium (^{2}H) NMR spectrum of 1-9d_2.

assumed to H3, H7 would be at 6.16ppm. Both possibilities are reasonable because both H7 and H3 are three bonds away from the Pt nucleus and should have a similar coupling constant with the platinum.)

Why does H3 not couple to H2 even though they are only three bonds away from each other? This question could not be answered with certainty until the X-ray crystal structure of 1-9 was obtained.

Crystal Structure of 1-9

X-ray quality crystals of 1-9 were obtained by slow evaporation from a mixture of THF (tetrahydrofuran) and hexane. The structure of 1-9 is represented in Fig.2-8, and important bond lengths and bond angles are listed in Table 2-1.

From these data, it is clear that the bond lengths of C(1)-C(2), C(1)-C(7), C(3)-C(4) and C(5)-C(6) are in the region expected of double bonds, while C(2)-C(3), C(4)-C(5) and C(6)-C(7) are in the single bond region. The angle of C(2)-C(1)-C(7) is 134.9(9), very close to the theoretical value (136.4°) of 1,2,4,6-cycloheptatetraene determined by INDO calculations.[25] The bond length of C(1)-C(2) is longer than C(1)-C(7). This can be explained by back bonding of a Pt "d" orbital into the π anti bonding orbital of the C(1)-C(2) double bond. The data in Table 2-1 and the fact that the seven-membered ring is bent unequivocally prove that the

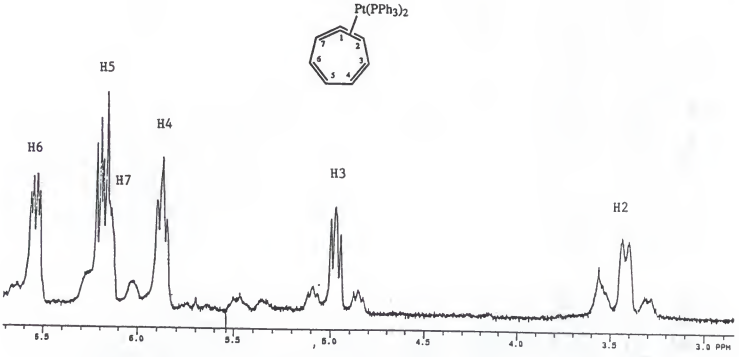


Fig.2-7. The chemical shifts of the six protons on the seven-membered ring of 1-9.

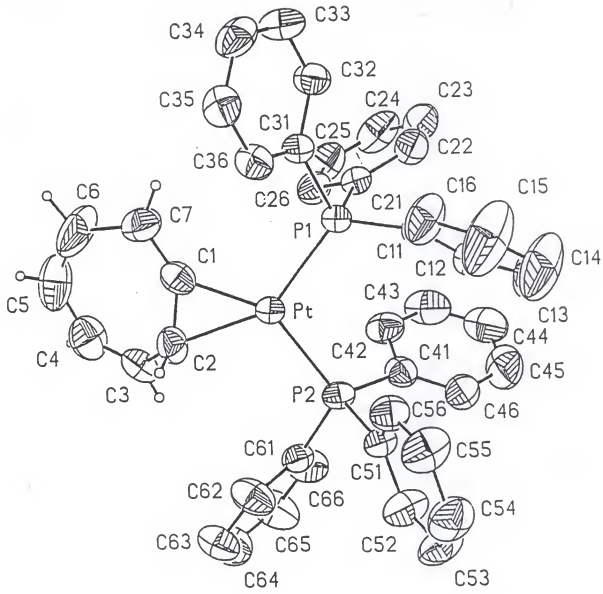


Fig.2-8. Molecular structure of 1-9.

Table 2-1. The important bond lengths(Å) and bond angles (°) of 1-9

Pt-P(1)	2.287(2)	Pt-P(2)	2.299(2)
Pt-C(1)	2.000(7)	Pt-C(2)	2.111(8)
C(1)-C(2)	1.365(11)	C(1)-C(7)	1.350(10)
C(2)-C(3)	1.429(15)	C(3)-C(4)	1.321(15)
C(4)-C(5)	1.411(15)	C(5)-C(6)	1.355(20)
C(6)-C(7)	1.407(15)		
P(1)-Pt-P(2)	105.5(1)	P(1)-Pt-C(1)	106.0(2)
P(2)-Pt-C(1)	148.2(2)	P(1)-Pt-C(2)	144.7(2)
P(2)-Pt-C(2)	109.7(2)	C(1)-Pt-C(2)	38.7(3)
Pt-C(1)-C(2)	75.0(4)	Pt-C(1)-C(7)	141.5(6)
C(2)-C(1)-C(7)	134.9(9)	Pt-C(2)-C(1)	66.3(5)
Pt-C(2)-C(3)	128.4(5)	C(1)-C(2)-C(3)	120.4(7)
C(2)-C(3)-C(4)	124.6(9)	C(3)-C(4)-C(5)	128.1(12)
C(4)-C(5)-C(6)	129.4(11)	C(5)-C(6)-C(7)	125.3(9)
C(1)-C(7)-C(6)	121.7(9)		

seven-membered ring in complex 1-9 is in an allene form, not only in solution but also in solid state.

The Pt atom is involved in asymmetric bonding with the C and P atoms, respectively. The bond length of Pt—C(1) is shorter than Pt—C(2) [2.000(7) Å and 2.111(8) Å, respectively]. This difference in bond lengths is the result of a difference in the bonding environments around the two C-atoms. Carbon atom C(1) is slightly more electronegative than C(2) due to an extra π-bond on C(1). Consequently, C(1) exerts a slightly stronger *trans* influence than C(2) by lengthening bond Pt—P(2) [2.299(2) Å compared to 2.287(2) for Pt—P(1) Å]. The Pt atom lies in the plane of coordination which forms an angle of 131.5(6)° with the plane of atoms C(1)-C(2)-C(3)-C(7). It is important to notice that the torsion angle H(2)-C(2)-C(3)-H(3) is 83(8)°; close to 90°, which explains why there is no coupling between H2 and H3 in the ^{1}H COSY NMR(Fig.2-2).[26]

CHAPTER 3
FLUXIONALITY OF (1, 2-η^2-
CYCLOHEPTATETRAENE)BIS(TRIPHENYLPHOSPHINE)PLATINUM

Introduction

There are many kinds of fluxional processes in organometallic complexes.[27-37] The process we are interested in in this Chapter is the migration of the $Pt(PPh_3)_2$ moiety in 1-9 between the two allene double bonds (Eq.3-1).

1-9 1-9

Eq.3-1

The first such fluxional process of a transition metal allene complex in which the ligand-metal interaction alternates between the two orthogonal π bonds of the allene system was observed by R. Ben-Shoshan and R. Pettit.[38]

Since then, this phenomenon has been observed in several kinds of metal allene complexes such as Fe(0)[39] and Fe(II),[39] Pd(0)[40] and Pt(II),[41,42] but, to our knowledge, no fluxional

process has been reported in a Pt(0) allene complex.[43] The method previously used to detect fluxionality in metalloallene complexes has been NMR line shape analysis (LSA), in which the temperature dependence of peak broadness and the coalescence of these peaks at a certain elevated temperature are studied. However, this method is limited.

In the 1970s and 1980s, several new dynamic NMR techniques were developed. One is spin saturation transfer (SST).[44] Another is 2D NMR such as NOESY[45] and EXSY.[46] The advantages of these techniques are that they can detect somewhat slower exchange processes than LSA.

Detecting the Fluxional Process of 1-9

LSA was first tried to detect the fluxional process of 1-9. Toluene-d_8 was used as the solvent because 1-9 is more stable in toluene than in chloroform-d_1. Also toluene has a higher boiling point than chloroform. However, even when 1-9 was heated to 105°C (at this temperature, 1-9 decomposes very rapidly), no coalescence between the peaks of H2 and H7, or H3 and H6, or H4 and H5 could be detected. Furthermore, due to extensive coupling, these proton peaks are too broad for meaningful line shape analysis (LSA). (It is interesting to note that heating caused the chemical shift of H6, H7, and H2 to move up-field about 0.1 ppm, while the chemical shift of H3, H4 and H5 remained almost unchanged. The reason for this is not clear).

The Principal of SST

Because LSA could not detect a fluxional process, the SST technique was tried.

The basic idea behind SST is, in short, to saturate (or invert) one of the exchanging spin resonances and observe the effect on the intensities of other spin resonances.

Technically, there are several ways to perform SST experiments. We used an arrayed difference spectrum, i.e. we subtracted a perturbed free induction decay (FID) from an unperturbed FID. The unperturbed FID gives a normal NMR spectrum. The perturbed FID is made up by the following pulse sequence (Fig.3-1)

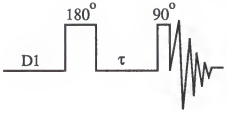


Fig.3-1. Pulse sequence used to make a perturbed FID.

The 180° pulse in Fig.3-1 is selective and only inverts the spin of a specific proton (for example X). The perturbed FID, therefore, will give a negative peak only to the proton X. If there is an exchange process between proton X and a

second proton (for example A), the spin negative protons from X will transfer to the environment of proton A and, at the same time, spin positive protons from A will transfer to the environment of proton X. As a result, this process will decrease the peak intensity of proton A. But the intensities of the rest of the proton peaks will remain unchanged. Therefore, after subtracting the two FIDs, all of the proton peaks will cancel, except proton X which is directly subjected to the 180° pulse and proton A which is affected by the exchange process (Fig.3-2).

The τ in the Fig.3-1 is the time allowed for proton X and A to transfer to each other's enviornments. During this time, spin negative protons will relax to their normal spin states at the rate of T_1^{-1}, where T_1 is the spin lattice relaxation time. If the τ is small, spin negative proton X does not have enough time to transfer to proton A. Therefore, proton A is not affected significantly and its peak intensity in the difference spectrum will be weak while the peak intensity of proton X will be strong. If the τ is too large, proton X will relax to its normal spin positive state and no negative spin will be transferred between proton X and proton A. In this case the peak intensities of both proton A and proton X will be equal to zero in the difference spectrum. Therefore, as τ increases from zero to infinity, peak A will go through a maximum intensity, while the peak intensity of X will decrease to zero (see Fig.3-2 for an example).[47]

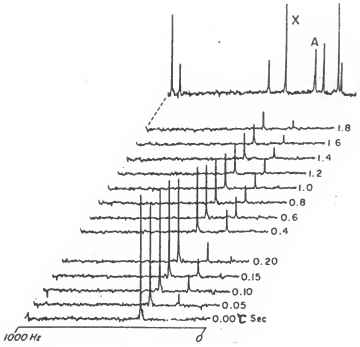


Fig.3-2. An example of the arrayed difference spectrum. [Spin X is directly subjected to 180° selective pulse; Spin A is exchanging with X, τ=0.00-1.8 sec.(11 values)].

Results of SST Experiments

SST experiments were conducted at 60°C, 80°C and 90°C. The results obtained at 80°C are shown in Fig.3-3 where exchange between H2 and H7 is obvious. Similar exchange has also been found between H3 and H6, and between H4 and H5. All of these results indicate that the $Pt(PPh_3)_2$ moiety is moving from one allene double bond to the other allene double bond.

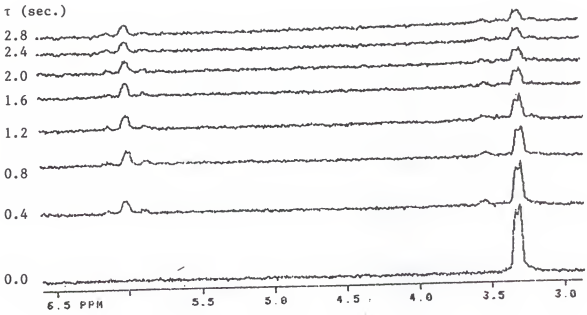


Fig.3-3. Effect on H7 when the spin of H2 is inverted at 80°C with different delay times.

From the above difference spectra, detection of fluxionality is qualitatively obvious, but precise calculation of the fluxional rate constant is very complicated.[33] However, in this kind of system, reliable estimates of rate constants can be obtained by applying Dahlquist and coworkers' approximation.[48] For 1-9 this leads to the following equation:

$$\ln[(X+A)/(X-A)]=2k\tau$$

X and A are the peak intensities of H2 and H7, respectively; k is the fluxional rate constant; and τ is the allowed transferring time.

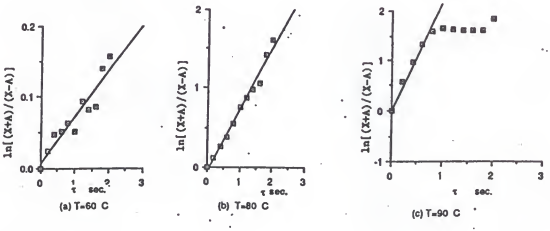


Fig.3-4. ln[(X+A)/(X-A)] versus τ.
a) At 60°C; b) At 80°C; c) at 90°C.

Three plots are showed in Fig.3-4, which were obtained at 60°C, 80°C, and 90°C respectively. At 60°C, the fluxional process is still slow; large error is thus introduced in peak intensity measurements leading to the scatter in Fig.3-4 (a). At 80°C, the fluxional process is rapid in terms of SST detection, therefore, the points show good linearity. At 90°C, a flat curve occurs when τ is larger than one second. It

is not clear what causes this abnormal deviation, but, at 90°C, decomposition of 1-9 becomes significant. For large τ, it takes longer to acquire a spectrum, and changes in concentration would be expected to affect the intensities severely. The values of X and A in the above equation, therefore, may not represent the true intensities of H2 and H7 at long delay time.

From the linear portions of the plots in Fig.3-4, rate constants k of 0.033 sec^{-1} at 60°C, 0.390 sec^{-1} at 80°C, and 0.990 sec^{-1} at 90°C were obtained. From the Arrhenius plot in Fig.3-5, the following activation parameters were obtained $\Delta H^{\neq}$=26.8±1.3 Kcal/mole and $\Delta S^{\neq}$=13.1±1.3 eu.

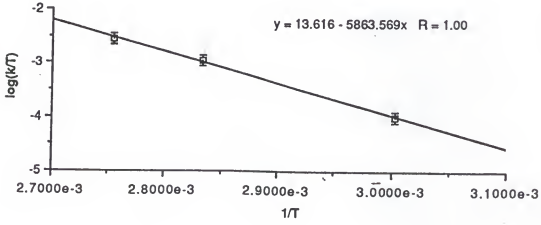


Fig.3-5. log(k/T) versus 1/T.

Mechanistic Studies on the Fluxional Process of 1-9

There are three possible mechanisms for the fluxional process of 1-9. One is intermolecular; two are intramolecular (Fig.3-6). Based on the fact that platinum has about 33.8% of ^{195}Pt isotope which has a spin of 1/2, the inter- and intramolecular mechanisms can be differentiated.

Principle

The proton resonances of H2, H3 and H7 in Fig.2-1 have a central peak and two satellite peaks. The satellite peaks represent the molecules which contain the ^{195}Pt isotope, while the central peaks represent the molecules which contain the rest of the platinum isotopes (for the sake of brevity, they will be referred to as $^{\circ}Pt$). In other words, the central peaks and the satellite peaks represent isotopically different molecules.

If the fluxional process is intramolecular, and if only the central peak of H2 is irradiated, then the saturated spin of H2 can be transferred only to the central peak of H7. As a result, in a difference spectrum, only the central peak of H2 and H7 will appear. If the process is intermolecular, when the central peak of H2 is irradiated, both the central peaks and the satellite peaks of H2 and H7 will appear in the difference spectrum, because in the fluxional process, when $^{\circ}Pt(PPh_3)_2$ leaves the cycloheptatetraene, both $^{\circ}Pt(PPh_3)_2$ and

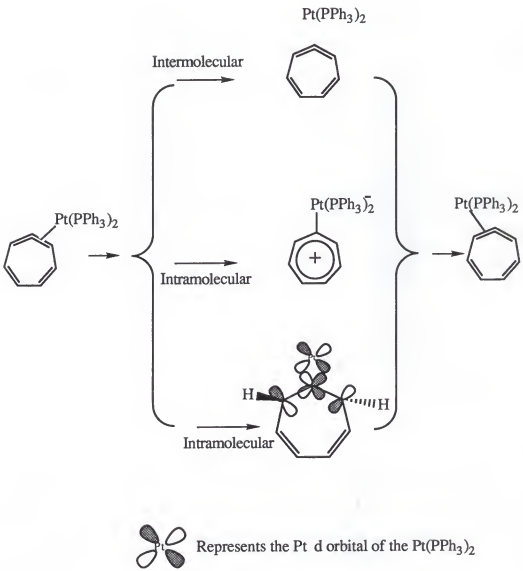


Fig.3-6. Three possible mechanisms of the fluxional process.

$^{195}Pt(PPh_3)_2$ can recoordinate. Furthermore, they can coordinate to either one of the two allene double bonds.

Experimentally, the irradiation at the central peak of H2 must not affect the two satellites; otherwise, both the satellite peaks and the central peaks of H2 and H7 will appear in the difference spectrum even if the fluxional process is intramolecular. This requires the irradiation power to be weak and only partially saturate the central peak.

Procedure and Results

The above discussion suggests that a proper irradiation power is the key to the success of this experiment. In order to find this irradiation power, the central peak of H2 was first irradiated at room temperature where the fluxional process is so slow on the NMR time scale that it can not be detected by SST. If the irradiation power is proper, only the the central peak of H2 should be seen in the difference spectrum. If the satellite peaks of H2 also appear, the irradiation power must be too strong and needs to be further reduced. By trial and error, it was finally found that a decoupler low power (DLP) of 35 (about 0.5 watt), led only to the central peak of H2 with no detectable satellite peaks (Fig.3-7b). The temperature was then increased to 80°C where fluxionality was known to be rapid. To ensure that the room temperature control experiment is valid at 80°C, the two positions, x (3.53 ppm) and y (3.05 ppm) (see Fig.3-7a) were

irradiated. The chemical shift difference between x and the left satellite peak of 0.12 ppm is equal to the chemical shift difference between this satellite peak and the central peak of H2. Similarly, the position y is separated from the high field satellite peak. Irradiation of these two positions with an irradiation power of DLP=35 showed no effects on the two satellite peaks. This result confirmed that the irradiation power is weak enough to avoid leakage to the satellites if it is applied to the central peak of H2 even at 80°C. After this double check, this irradiation power was then applied to the central peak of H2 at 80°C and the spectrum in Fig.3-7c was obtained. From Fig.3-7c, it was found that H2 and H7 both have central and satellite peaks. This means that the fluxional process must be an intermolecular one.

Based on the natural abundance of ^{195}Pt isotope, the intensity of the satellite peak versus the central peak should be about 1:4 (see Fig.3-7a), but in Fig.3-7c the intensities of the satellite peaks for H7 are less than this ratio. This suggests that the fluxional process may not be completely intermolecular; some intramolecular or an equivalent process may also be occurring.

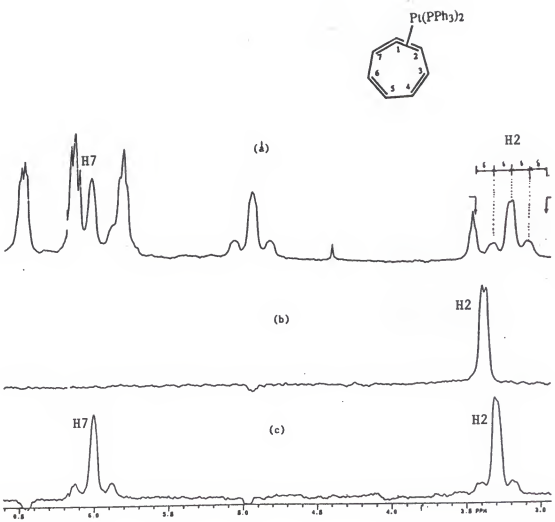


Fig. 3-7. Test the mechanism of the fluxional process. (a) C_7H_6 region of the ^1H NMR spectrum of 1-9 at 80°C. (b) Difference spectrum when only the central peak of H2 is irradiated at room temperature. (c) Difference spectrum when only the central peak of H2 is irradiated but at 80°C.

NOESY and EXSY Experiments

As mentioned in the introduction to this chapter, 2D NOESY and EXSY NMR are also very good methods to study the fluxional processes. NOESY is used for ^{1}H NMR and EXSY can be used for ^{31}P NMR. The cross peaks in these spectra represent the exchanges between two resonances. From the NOESY spectrum of 1-9 at 80 °C (Fig.3-8), we can clearly see that H2, H3 and H4 exchange with H7, H6 and H5, respectively. It was also found that the two satellite peaks of H2 and H3 are exchanging. This actually is caused by the relaxation of ^{195}Pt. In addition to this, there are crosspeaks between the downfield satellite peak of H3 and its central peak. This means that there is an exchanging process between the satellite peak and its central peak. This also supports the conclusion that the exchange and the fluxional process is intermolecular(Because of decomposition of 1-9 at high temperature and poor mixing time, the cross peaks between the upfield satellite peak and the central peak of H2 and H3 cannot be detected in this NOESY experiment).

To determine if the fluxional process is an inter- or intramolecular mechanism, ^{31}P EXSY is, in principle, better than ^{1}H NOESY because the coupling constants between platinum and phosphorous are much larger than those between platinum and hydrogen. Therefore the crosspeaks between a satellite peak and the central peak in the EXSY spectrum will be less affected by the baseline noise. Unfortunately, it was not

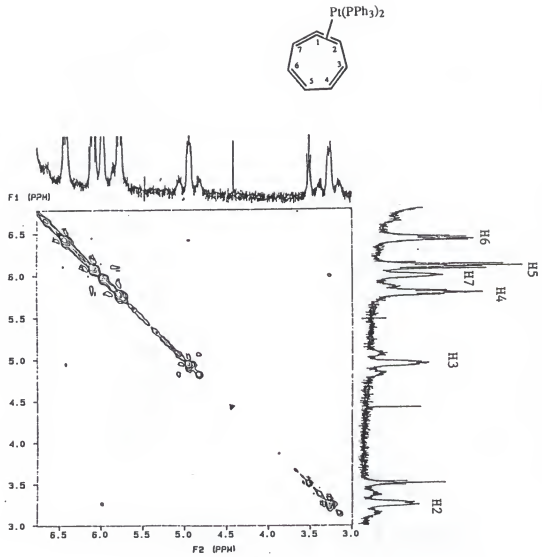


Fig.3-8. The NOESY spectrum of 1-9.

possible to obtain a good EXSY spectrum due to significant decomposition of 1-9 during the prolonged acquisition time required for the EXSY experiment.

CHAPTER 4
PLATINUM(II) CYCLOHEPTATRIENYLIDENE COMPLEX

Introduction

The seven-membered ring intermediate, C_7H_6, can have two forms, the allene form 4-1 or the carbene form 4-2. It has been well established that the allene form 4-1 is energetically preferred over its planar valence isomeric carbene form 4-2.[49-52]

Eq.4-1

4-1 4-2

In transition metal complexes, however, the situation is quite different.

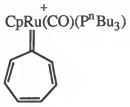
In complexes of 1-1, 1-4, 1-7 and 1-8, C_7H_6 exists exclusively in the carbene form, but in complex 1-9, the allene form is the ground state. A comparison of complexes of 1-1,[19] 1-4,[20] 1-7[19] and 1-8[20] with 1-9 shows that each of the metals in the 1-1, 1-4, 1-7 and 1-8 has six d electrons, while the metal in 1-9 has ten d electrons.

1-1

Fp=(η^5-C_5H_5)Fe(CO)$_2$

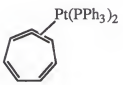
1-4

Rp=(η^5-C_5H_5)Ru(CO)$_2$



1-7

1-8



1-9

Winchester[21] studied the orbital interaction of Fp^+ and $Pt(PH_3)_2$ fragments with the allyl fragment 4-3 and its valence isomeric allene form 4-4 (note the allene is bent) by using molecular orbital calculations at the extended Huckel level. The results are shown in Fig.4-1, Fig.4-2, Fig.4-3 and Fig.4-4.

4-3

4-4

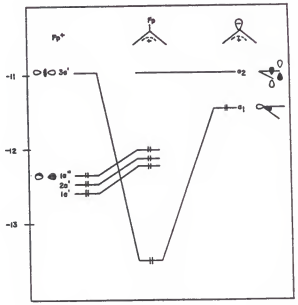


Fig. 4-1. Orbital interaction between Fp^+ and 4-3.

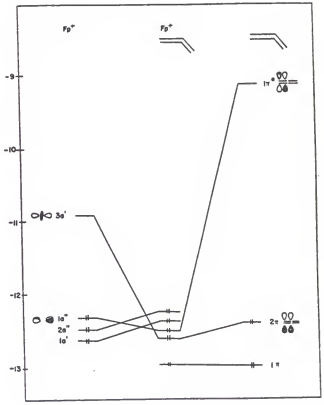


Fig. 4-2. Orbital interaction between Fp^+ and 4-4.

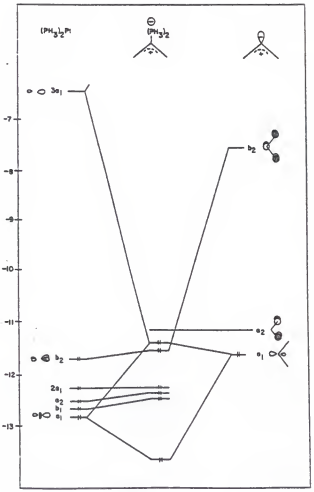


Fig. 4-3. Orbital interaction between $Pt(PH_3)_2$ and 4-3.

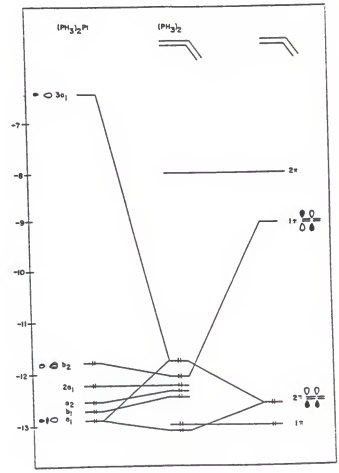
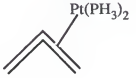


Fig. 4-4. Orbital interaction between $Pt(PH_3)_2$ and 4-4.

One remarkable result from these calculation is that the HOMO of 4-3 (a_1 orbital in Fig.4-1) is energetically very close to the LUMO of Fp^+ (3a' orbital), therefore, the HOMO and the LUMO interact strongly and the resulting bonding orbital is stabilized by approximately 2 eV. In contrast, the HOMO of 4-4 (2π orbital in Fig.4-2) and the LUMO of Fp^+ are on quite different energy levels. Their interaction gives a bonding orbital stabilized by only 0.5 eV. Therefore, it is possible that the strong interaction between the LUMO of a metal containing six d electrons as Fp^+ and the HOMO of the 4-2 causes the C_7H_6 in 1-1 to prefer the carbene form 4-2 when it is coordinated to that metal.

The $Pt(PH_3)_2$ fragment has a Pt(0) metal which contains ten d electrons. The LUMO of $Pt(PH_3)_2$ is therefore very high. A comparison of Fig.4-3 with Fig.4-1 shows that the interaction between the LUMO of $Pt(PH_3)_2$ and the HOMO of 4-3 is weak and no longer dominates the relative stability between complexes 4-5 and 4-6. This may explain why C_7H_6 still exists in the allene form 4-1 when it is coordinated to $Pt(PPh_3)_2$, which has ten d electrons.

4-5



4-6

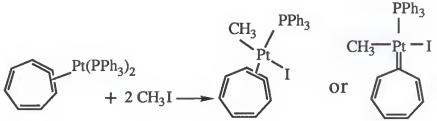
Winchester's study leaves one interesting question: which form will C_7H_6 prefer when it is coordinated to a metal containing EIGHT d electrons. From Fig.4-3, we can see that removing two electrons from $Pt(PH_3)_2$ will make the b_2 orbital the LUMO of $Pt(PH_3)_2$. The b_2 orbital of $Pt(PH_3)_2$ is very close to the HOMO of the 4-3. This, however, does not necessarily mean that strong HOMO-LUMO interaction will occur because the symmetry of these two orbitals does not match.

A four coordinated Pt(II) C_7H_6 complex may be therefore a good complex to study. Platinum (II) contains eight d electrons and the orbital symmetry in the four coordinated Pt(II) complex should be different from that in a three coordinated Pt(0) as in 1-9.

Searching for a Four Coordinated Pt(II) C_7H_6 Complex

Our first effort was to synthesize complex 4-7 or 4-8 by the reaction of Eq.4-2.

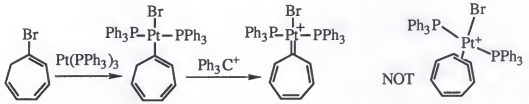
Eq.4-2



1-9 4-7 4-8

This reaction did not produce the desired product, 4-7 or 4-8. It seems that the C_7H_6 dissociated from the platinum and formed a complicated mixture of products. In our second effort, we tried to abstract one hydride from the seven-membered ring of complex 4-9 (Eq.4-3). This was successful and complex 1-12 was isolated but not its allene analogue 4-10.

Eq.4-3



2-1 4-9 1-12 4-10

Synthesis of Complex 1-12

Complex 1-12 was prepared by slow addition of 1.5 equiv. of Ph_3C^+ BF_4^- to 1 equiv. of 4-9 in methylene chloride solution at room temperature. At first, the color of the solution changed to bloody red, then it slowly faded and finally became greenish yellow. Complex 1-12 was precipitated as a greenish yellow solid by adding an excess of hexane solvent. Attempts to obtain a single crystal suitable for X-ray diffraction by recrystallization from CH_2Cl_2/hexane/ether

solution failed because the resulting crystals are very sensitive to loss of solvent.

The NMR spectra are consistent with structure 1-12. For example, The ^{31}P NMR (Fig.4-5) shows only a singlet (with platinum satellites) rather than a doublet of doublets as is found for allene complex 1-9. In the ^{1}H NMR spectrum, the protons on the seven-membered ring of 1-12 (Fig.4-6) are similar to those of 1-1, 1-4, 1-7 and 1-8 rather than 1-9.

In 1-12 the seven-membered ring is symmetrical; therefore it should have three kinds of proton resonances. In Fig.4-6, two of the three are apparently displayed, but the third one is buried in the phenyl region. With a COSY spectrum, the chemical shift of the third resonance can be easily determined (Fig.4-7). The doublet at 8.89 ppm in the Fig.4-6 has the typical platinum satellite peaks, so it can be assigned as H_{α}. According to the COSY spectrum (Fig.4-7), H_{β} and H_{γ} can be assigned at 7.42 ppm and 8.09 ppm, respectively.

The ^{13}C NMR spectrum of 1-12 is shown in Fig.4-8. The assignment of the carbon atoms on the seven-membered ring was done by a C-H heteronuclear chemical shift correlation 2D NMR (Fig.4-9). Assignments for the phenyl carbons are based on the empirical rule that in Pt(II) bis(triphenyl)phosphine complexes, if the two PPh_3 groups are trans to each other, all the phenyl carbons will appear as triplets because of their coupling to the two phosphorus atoms.[53]

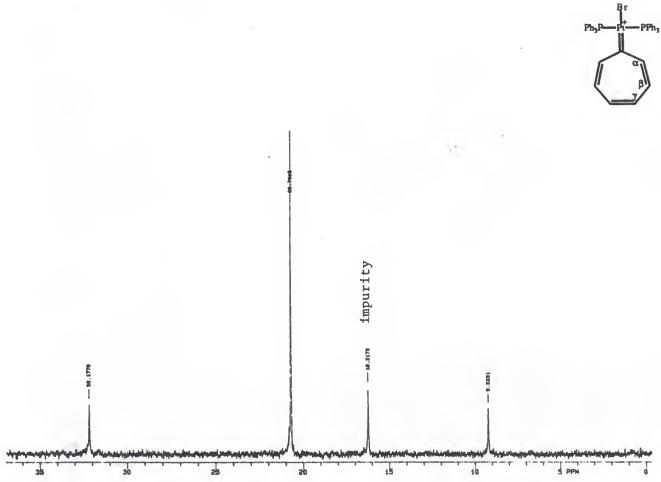


Fig.4-5. The ^{31}P NMR spectrum of 1-12.

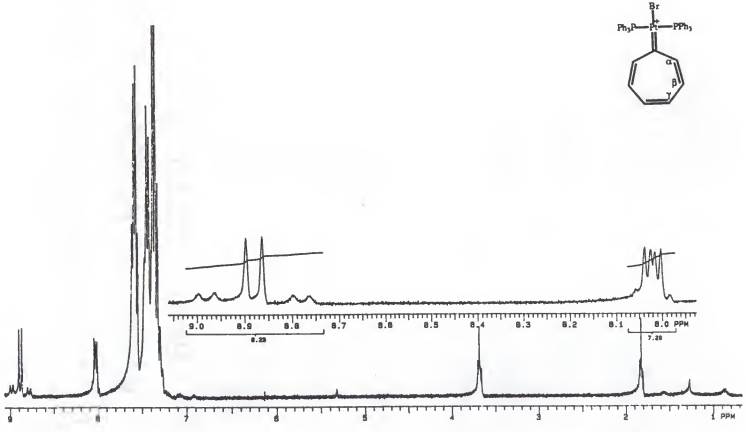


Fig.4-6. The ^{1}H NMR spectrum of 1-12.

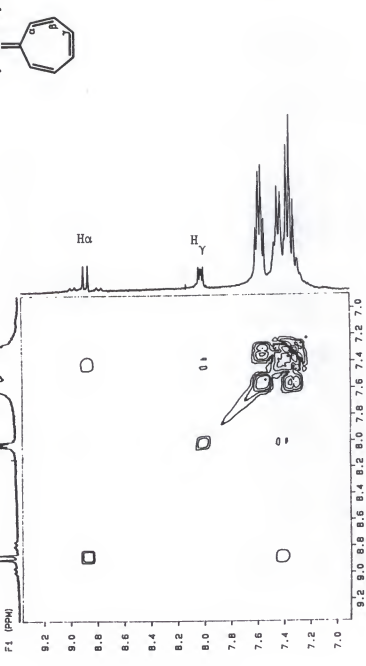


Fig.4-7. The COSY spectrum of 1-12.

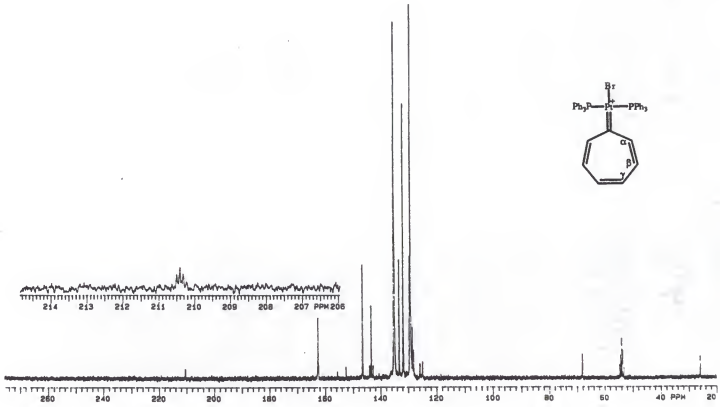


Fig.4-8. The ^{13}C NMR spectrum of 1-12.

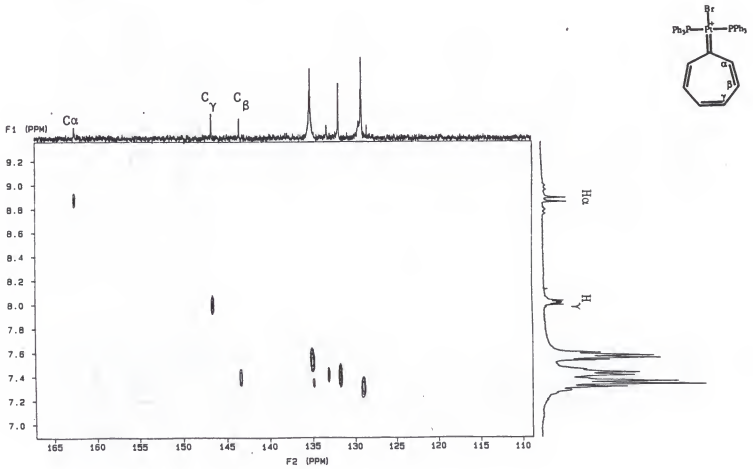
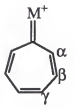


Fig.4-9. The carbon-hydrogen heteronuclear correlation 2D NMR spectrum of 1-12.

The ^{1}H NMR data of 1-1, 1-4, 1-7, 1-8 and 1-12 are listed in Table 4-1 and the ^{13}C NMR data of 1-1, 1-4, 1-7 and 1-12 are listed in Table 4-2. From Table 4-1 and Table 4-2, it was found that for all the complexes, changes of chemical shift are $H_\alpha > H_\gamma > H_\beta$ and $C_\alpha > C_\gamma > C_\beta$.

All the carbene complexes listed in Table 4-1 and Table 4-2 are formed by the interaction between a metal fragment and a tropylium fragment; and can be represented as 4-11. A simple Huckel molecular orbital calculation[54] shows



4-11

that the LUMO of the tropylium ion has the coefficient of 0.12 for its C_α, 0.48 for C_β and 0.33 for C_γ. Based on these orbital coefficients, if the central metal donates electron density back to the π-system of the tropylium ion, the electron density will be distributed so that, among the α, β and γ positions, the β position will receive the largest portion of the electron density and the α position will receive the smallest portion of the electron density. This conclusion is consistent with the proton and carbon NMR data. Here we clearly see the carbene 4-1 acting as a σ electron donor and a π electron acceptor simultaneously.

Table 4-1. The ^{1}H NMR data of complexes 1-1, 1-4, 1-7, 1-8 and 1-12 (ppm).

Complex	H_{α}[a]	H_{β}	H_{γ}
1-12	8.89 (11.7)	7.42	8.09
1-1	10.01 (10.0)	8.1	8.48
1-4	9.50 (10.0)	8.13	8.55
1-7	9.1 (11.0)	7.1	7.7
1-8	9.96 (10.0)	7.7[b]	8.1[b]

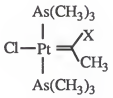
a. The numbers in parentheses are the $^{3}J_{H-H}$ coupling constant. b. The relative assignment of these two resonances needs to be further confirmed.

Table 4-2. The ^{13}C NMR data of complexes 1-1, 1-4, 1-7 and 1-12 (ppm).

Complex	C_{carb}[a]	C_{α}	C_{β}	C_{γ}
1-12	210.5	162.5	143.5	146.5
1-1	242.3	170.0	138.2[b]	148.3[b]
1-4	223.6	170.1	140.9	149.2
1-7	256.2	168.1	135.2	145.5

a. C_{carb} represents the carbon atom directly bonded to metal (carbene carbon). b. The relative assignment of these two resonances needs to be further confirmed.

The chemical shifts and $^{1}J_{Pt-C}$=969.0 Hz of the complex 1-12 all fall in the region reported for carbene complexes 4-17.[55,18] This suggests that 1-12 is a Fisher type carbene, not a Shrock type carbene.



X=OR or NR_2

4-17

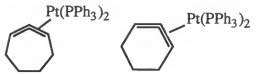
The ^{195}Pt NMR chemical shift (-4095 ppm) of the 1-12 is remarkably downfield from the chemical shift of the 4-9 (-4439 ppm) even though both are Pt(II) atoms. This suggests that large amount of the electron density has been transferred to the seven-membered ring system in complex 1-12. The ^{31}P NMR of the 1-12 (20.7 ppm $^{1}J_{Pt-P}$=2777 Hz), however, does not show significant differences from its precursor 4-9(21.3 ppm, $^{1}J_{Pt-P}$=3215 Hz).[21] This may suggest that the chemical shift in ^{31}P NMR is not very sensitive to the changes of the electronic environment.

CHAPTER 5
PREPARATION OF PLATINUM (0) COMPLEXES OF CYCLOHEPTADIENE, CYCLOHEXADIENE, CYCLOHEPTYNE AND CYCLOHEXYNE.

Introduction

In Chapter 3, spin saturation transfer was used to unequivocally demonstrate that fluxionality in 1-9 is intermolecular; i.e. the process requires dissociation of platinum from the allene. Furthermore, from rates at different temperatures, activation parameters for this process were determined. In Chapter 4, it was shown that reducing the electron density on the central metal [change from Pt(0) to Pt(II)] makes the carbene complex 1-12 more stable than its allene counterpart 4-10.

In 1972, Visser reported preparation of the bistriphenylphosphine platinum complex of 1,2-cycloheptadiene 5-1.[6] Inasmuch as a study of fluxionality in this allene complex would provide a direct measure of the effect of two additional double bonds on the allene π-bond



5-1 5-2

strength, attempts to reproduce Visser's preparation of 5-1 for spin saturation transfer studies were undertaken.

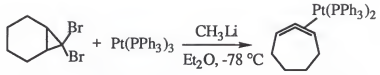
To assess the effect of increasing ring strain on the fluxional process, preparation of the six-membered complex 5-2 was also attempted although it was recognized from the outset that chances of success were poor since Visser had previously reported that his attempts to prepare this complex had faied.[6] However, although this was borne out, while attempting to optimize the yield of 5-1 and prepare 5-2, it was discovered that substituting lithium diisopropylamide for potassium *tert*-butoxide provided a convenient method to prepare bistriphenylphosphine platinum complexes of both cycloheptyne and cyclohexyne. This discovery led to the preparation of the first transition metal complex of tropyne. This will be discussed in Chapter 7 and Chapter 8.

Synthesis and Fluxionality of the Complex 5-1

Preparation of 5-1

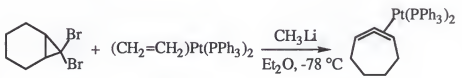
Preparation of complex 5-1 has been reported by Visser,[6] but no preparation details were provided. We tried to prepare 5-1 by the following four reactions (Eq.5-1, Eq.5-2, Eq.5-3 and Eq.5-4).

Eq. 5-1



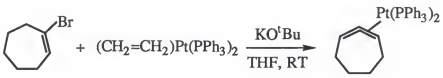
5-3 5-1

Eq. 5-2



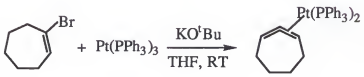
5-3 5-4 5-1

Eq. 5-3



5-5 5-4 5-1

Eq. 5-4



5-5 5-1

While Visser rported conditions in Eq.5-3, we found that the reaction in Eq.5-4 produced 5-1 in higher yield. The reactions in Eq.5-1 and Eq.5-2 did not produce complex 5-1.

In the ^{1}H NMR spectrum of complex 5-1 (Fig.5-1), the chemical shifts of the two allene protons are identical with those reported by Visser (He gave no other NMR data). The ^{31}P NMR (Fig.5-2) also shows resonances consistent with structure 5-1. There are two doublets: one at 30.6 ppm ($^{1}J_{Pt-P}$=3135 Hz, $^{2}J_{P-P}$=35 Hz), and one at 34.5 ppm ($^{1}J_{Pt-P}$=3171 Hz, $^{2}J_{P-P}$=35 Hz). The ^{195}Pt NMR spectrum of 5-1 (Fig.5-3) shows a doublet of doublets at -4939 ppm. All of these data are consistent with structure 5-1. Moreover, from Fig.5-2 and Fig.5-3, it is clear that there is another compound in addition to 5-1. This new material gives a singlet at 29.9 ppm ($^{1}J_{Pt-P}$=3263 Hz) in its ^{31}P NMR spectrum, and a triplet at -4698 ppm in its ^{195}Pt NMR spectrum. From these data, this compound must have two equivalent phosphorous atoms directly bonded to the platinum. The ratio of this compound (which was finally identified as the cycloheptyne complex 5-8) to complex 5-1 is about 1 : 4 based on the ^{31}P NMR spectrum (Fig.5-2). All attempts to separate this compound from 5-1 failed.

Properties of 5-1

Despite the presence of 5-8, it was still possible to study the fluxionality of 5-1. The fluxional process of 5-1 is very slow. By SST, no fluxionality could be detected below

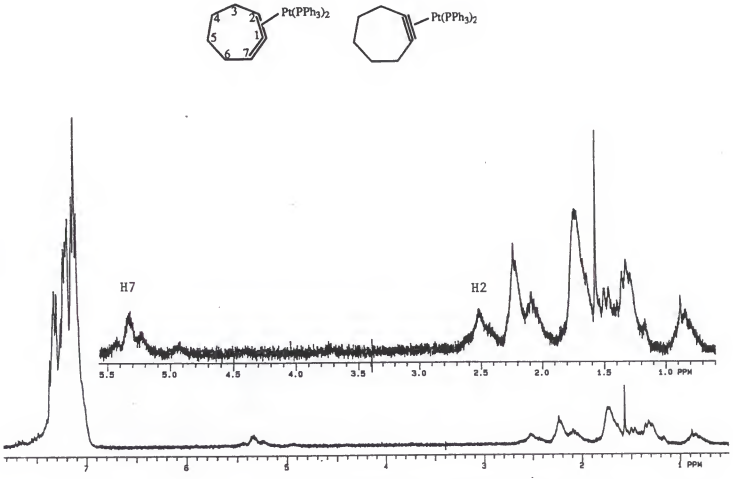


Fig.5-1. The ^{1}H NMR spectrum of complex 5-1 and 5-8.

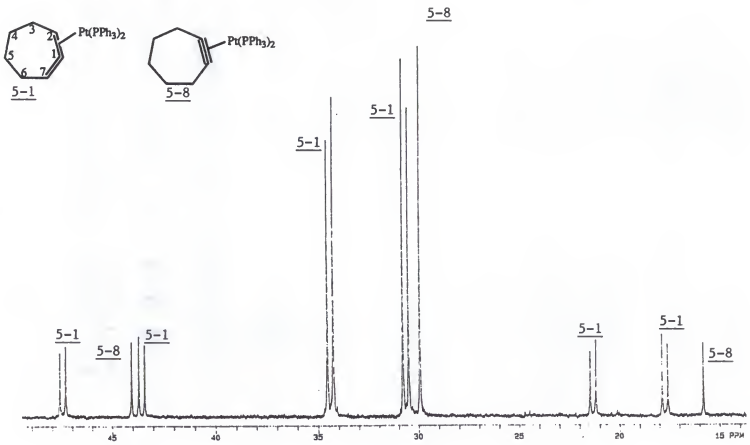
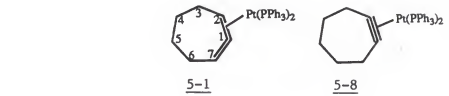


Fig.5-2. The ^{31}P NMR spectrum of complex 5-1 and 5-8.



5-1 5-8

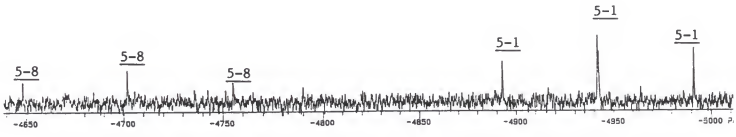


Fig.5-3. The ^{195}Pt NMR spectrum of complex 5-1 and 5-8.

100°C where the complex 5-1 begins to show significant decomposition. At this temperature, the fluxional process can barely be detected (Fig.5-4), but it is not fast enough to calculate the rate constant or activation parameters. This rate retardation, however, clearly indicates that removing two double bonds from the seven-membered ring of 1-9 strengthens the bonding between the allene double bond and the $Pt(PPh_3)_2$. There is additional evidence that supports this suggestion. For example, 1-9 decomposes at room temperature in $CDCl_3$ after 12 hours and in toluene-d_8 after two days, but 5-1 is stable in $CDCl_3$ for a week and no decomposition was found in toluene-d_8 for up to a month.

Because the crystal structure of 5-1 could not be obtained (distortion in the unit cell caused by co-crystallization of 5-8 precluded this), it was not possible to compare the bond distance between the Pt and the two vinylic carbons of the coordinated allene double bond in 5-1 with those in 1-9. However, a comparison of the ^{31}P NMR data of 1-9 and 5-1 gave us some information about this bonding. Like 5-1, 1-9 shows two doublets. The upfield doublet (27.3 ppm) exhibits a Pt-P coupling of $^1J_{Pt-P}$=3170 Hz and the downfield resonance (31.5 ppm) exhibits $^1J_{Pt-P}$=3266 Hz. These $^1J_{Pt-P}$ values of 1-9 are significantly larger than are the corresponding coupling constants of 5-1 (3135 and 3171 Hz, respectively). It has been well documented[56] that the $^1J_{Pt-P}$ values are affected by the bonding between the Pt and the ligand trans to the phosphorus (trans influence), the

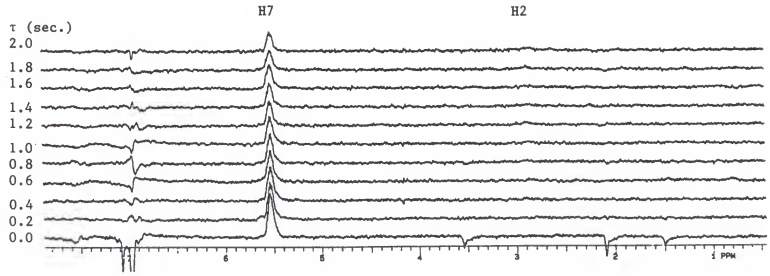


Fig.5-4. SST of Complex 5-1 at 100°C.

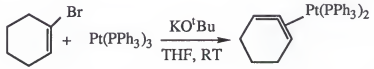
stronger the bond, the smaller the $^1J_{Pt-P}$ coupling. The relatively smaller $^1J_{Pt-P}$ in 5-1, therefore, suggests a relatively stronger bonding between the Pt and the allene double bond in 5-1.

Pt(0) Complexes of 1,2-Cyclohexadiene 5-2, Cyclohexyne 5-7 and Cycloheptyne 5-8.

There were two purposes for preparing complex 5-2: first, we wanted to compare the fluxionality of 5-2 with that of 5-1 and 1-9; second, to date the smallest reported cyclic allene transition metal complexes are seven-membered. To our knowledge, no complex of a six-membered cyclic allene has been reported. As mentioned in the introduction to this chapter, Visser et al. have tried to prepare 5-2 but failed.

We first tried to apply the reaction described in Eq.5-4 to the synthesis of 5-2 (Eq.5-5),

Eq.5-5

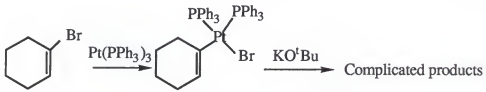


5-9 5-2

but, similar to Visser,we also failed. After carefully examining the reaction product, it was found that KO^tBu is not a strong enough base to remove HBr from 5-9 before platinum insertion (see Chapter 6) occurs to give 5-10 which

reacts with KO^tBu to give a complicated mixture of products (Eq.5-6). A stronger base was therefore sought.

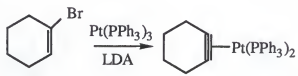
Eq.5-6



5-9 5-10

Of the bases tried, LDA (lithium diisopropylamide) was surprising in that the major product was found to be cyclohexyne complex 5-7 (Eq.5-7), and no allene complex 5-2

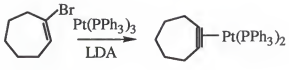
Eq.5-7



5-9 5-7

could be detected in the reaction mixture by ^{31}P NMR. Even more surprising was the finding that 1-bromocycloheptene 5-5 behaves similarly. Reaction of 5-5 with LDA and $Pt(PPh_3)_3$ gives only cycloheptyne complex 5-8 (based on the ^{31}P NMR spectrum of the reaction mixture); no allene complex 5-1 was detected (Eq.5-8). The cycloheptyne complex 5-8 was fully characterized.

Eq.5-8

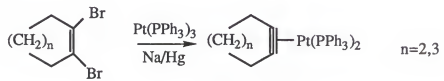


5-5 5-8

With an authentic sample of 5-8 in hand, it was possible to identify the unknown compound in Fig.5-2 and Fig.5-3 as 5-8.

Both 5-7 and 5-8 have been prepared by Bennett et al.,[57,58] but they used different reagents (Eq.5-9). The method reported here is new.

Eq.5-9



n=2, 5-7
n=3, 5-8

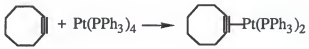
CHAPTER 6
STUDIES ON THE MECHANISM OF FORMATION OF PT(0) COMPLEXES OF CYCLOHEPTADIENE AND CYCLOHEPTATETRAENE

Introduction

Stabilization of highly strained cyclic alkynes or cyclic allenes by complexing them to Pt(0) is very common (see the references of Chapter 1), but the mechanisms of their formation remain unsolved.

Based on the fact that cyclooctyne Pt(0) complex 6-1 can be prepared by either direct reaction of cyclooctyne with $Pt(PPh_3)_4$ (Eq.6-1),[59] or generating cyclooctyne in situ by

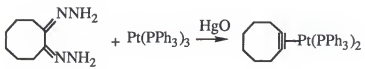
Eq.6-1



6-1

mercuric oxide oxidation of 1,2-cyclooctanedionebis(hydrazone) in the presence $Pt(PPh_3)_3$ (Eq.6-2),[57] Bennett initially proposed that the mechanism of

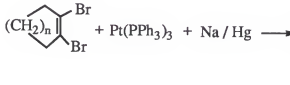
Eq.6-2



6-1

the formation of cyclohexyne Pt(0) complex 5-7 and cycloheptyne complex 5-8 involved trapping of transient cyclohexyne 6-2 and cycloheptyne 6-3 (trapping mechanism), as shown in Eq.6-3, because these two cyclic alkynes can be generated by alkali or alkaline-earth metal reduction of corresponding 1,2-dibromocycloalkenes.[57,58]

Eq.6-3

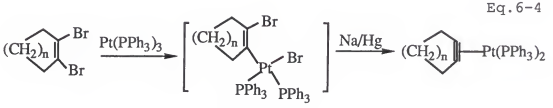


n=2, 6-2
n=3, 6-3

n=2, 5-7
n=3, 5-8

In discussing Bennett's work, Chisholm[60] proposed that the reaction goes first to the Pt(II) cis-insertion complexes 6-4 and 6-5, from which reduction occurs (Eq.6-4). We shall refer to this as the insertion mechanism.

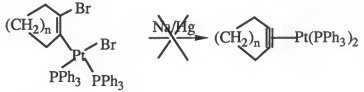
Eq.6-4



n=2, 6-4
n=3, 6-5

The possibility of the insertion mechanism for 5-7 and 5-8, however, was excluded by Bennett because he isolated Pt(II) cis-insertion complexes 6-4 and its five-membered ring analogue 6-6 and found that they cannot be reduced to Pt(0) complexes of cyclohexyne 5-7 and cyclopentyne 6-7 by sodium amalgam, Eq.6-5.

Eq.6-5

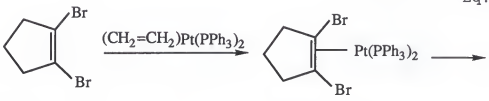


n=1, 6-6
n=2, 6-4

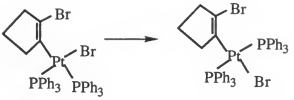
n=1, 6-7
n=2, 5-7

In his search for cyclopentyne Pt(0) complex 6-7, Bennett found that similar treatment of 1,2-dibromocyclopentene with sodium amalgam and $Pt(PPh_3)_3$ does not produce 6-7.[57] However, treating 1,2-dibromocyclopentene with $(CH_2{=}CH_2)Pt(PPh_3)_2$ alone produces a π-complex 6-8, which isomerizes successively to the Pt(II) cis- and trans-insertion complexes 6-6 and 6-9, respectivly (Eq.6-6).

Eq.6-6



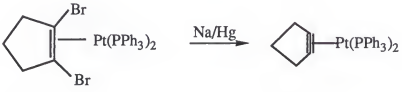
6-8



6-6 6-9

When 6-8 was isolated and treated with sodium amalgam, the cyclopentyne complex 6-7 was obtained (Eq.6-7).[9]

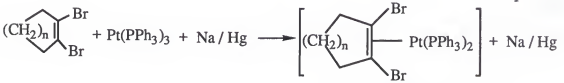
Eq.6-7



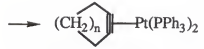
6-8 6-7

Based on these results, Bennett later strongly suggested that the six- and seven-membered ring analogues of 6-8, i.e. π-complex 6-10 and 6-11 are intermediates in the formation of the corresponding cyclic alkyne complexes 5-7 and 5-8 (Eq.6-8), even though he had not detected or isolated these intermediates. This mechanism will be referred to as the π-complex mechanism.

Eq.6-8



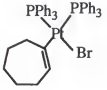
n=2, 6-10
n=3, 6-11



n=2, 5-7
n=3, 5-8

In contrast to complexes of strained cyclic alkynes, since Visser's first preparation of the Pt(0) complex 1,2-cycloheptadiene Pt(0) complex 5-1, and his suggestion that the reaction goes by the trapping mechanism,[6] no other comments about the mechanism of formation of transition metal complexes of strained cyclic allenes have been found in the literature.

In our preparation of 5-1 by the reaction in Eq.5-4, we discovered that about fifteen minutes after one equivqlent of 1-bromocycloheptene 5-5 (in THF) had been added to a THF solution of two equivalents of KO^tBu and one equivalent of $Pt(PPh_3)_3$, in addition to the the peaks of the desired product 5-1, the ^{31}P NMR spectrum of the reaction mixture also showed two doublets: one at 17.7 ppm ($^1J_{Pt-P}$=4742 Hz, $^2J_{P-P}$=13 Hz), the other at 18.6 ppm ($^1J_{Pt-P}$=1458 Hz, $^2J_{P-P}$=13 Hz). These two doublets resulted from the cis-insertion complex 6-12 (vide infra). As the reaction continued, 6-12 disappeared. This discovery aroused our interest in studying the mechanism of the formation of platinum complexes of strained allenes.

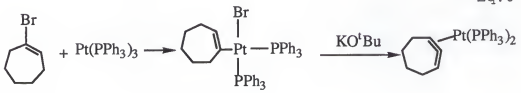


6-12

Reaction of 5-5 with $Pt(PPh_3)_3$ and KO^tBu

From the previous discussion, there are three mechanisms for the formation of 5-1 from 5-5 that need to be considered. One is simple elimination of HBr to give the allene that is then trapped (trapping mechanism). A second mechanism is analogous to Chisholm's proposal and is given in Eq.6-9 (insertion mechanism). A third possibility is

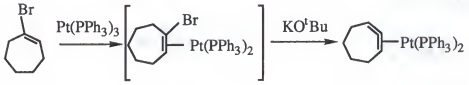
Eq.6-9



5-5 6-12 5-1

analogous to Bennett's π-complex mechanism for formation of cycloheptyne complex 5-8: this is given in Eq.6-10.

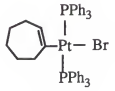
Eq.6-10



5-5 6-13 5-1

To distinguish between these possibilites, 5-5 was added to a benzene solution of $Pt(PPh_3)_3$ at room temperature. The color of the solution changed instantly from orange yellow to

yellow and, as mentioned above, the ^{31}P NMR spectrum showed that 6-12 was produced (Fig.6-1). This compound isomerized to its trans-isomer 6-14 (Fig.6-2),[21] but only slowly at room temperature in benzene, more rapidly in THF, and faster yet in methylene chloride. The slow isomerizaton permitted isolation of 6-12 by adding excess hexane to the benzene solution.



6-14

The vinyl proton (in CD_2Cl_2 at -20°C) of 6-12 appears at 5.62 ppm. The Pt-H coupling could not be determined because of the broadness of the resonance. One of the methylene protons appears at 2.58 ppm, the resonances of the rest of the nine methylene protons overlap in the region of 1-2 ppm. The ^{195}Pt NMR of 6-12 shows a doublet of doublets at -4567.6 ppm ($^1J_{Pt-P_1}$=1458 Hz and $^1J_{Pt-P_2}$=4751 Hz). The isomerization of 6-12 to its trans isomer 6-14 made it very difficult to assign resonances in ^{13}C NMR.

Reaction of 6-12 with KO^{t}Bu in THF gives no trace of allene complex 5-1; only a complicated mixture of products was obtained. This result excludes the insertion mechanism as a viable possibility for formation of 5-1.

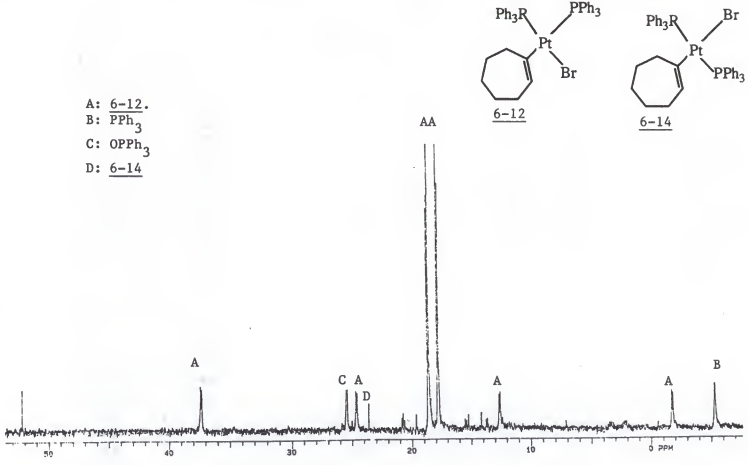


Fig.6-1. The ^{31}P NMR of the reaction mixture of 5-5 and $Pt(PPh_3)_3$ in benzene solution at room temperature.

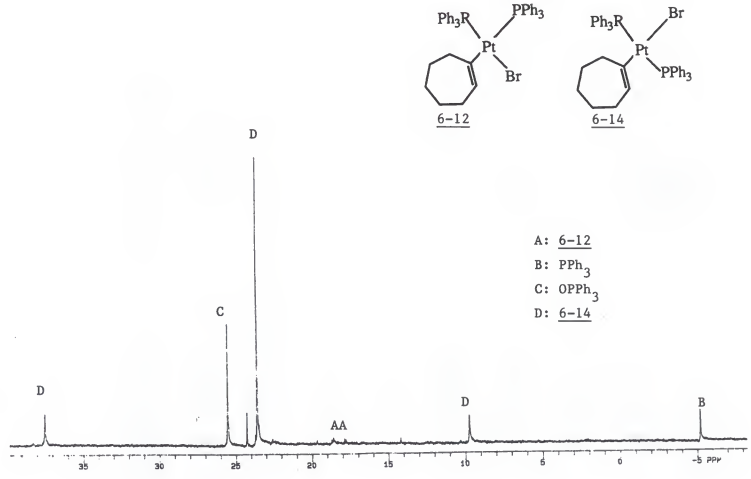
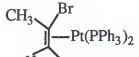
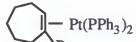


Fig.6-2. The ^{31}P NMR of the reaction mixture of 5-5 and $Pt(PPh_3)_3$ in benzene solution at room temperature after 72 hours.

In search for a possible π-complex mechanism, 5-5 was treated with $Pt(PPh_3)_3$ in THF at various low temperatures and the reaction was monitored by a kinetic ^{31}P NMR program. With this program, a set of Pre-Acquisition Delays (PAD) can be set, with values varying from several minutes to several hours. Acquisition automatically takes place after each time increment, and a series of spectra can be obtained with identical data processing parameters. From these spectra, changes in peak intensities can be determined as a function of time. Using this method at -30°C, a new species was detected that precedes 6-12 (Fig.6-3). By comparing the chemical shifts and the coupling constants of this species with those of 2-bromo-1-propene bis(triphenylphosphine)platinum 6-15 reported by Stang,[61] we suggest that this new material is the π-complex 6-13.



6-15



6-13

δ 23.9 ppm, $^1J_{Pt-P}$=3013 Hz, $^2J_{P-P}$=43 Hz
δ 27.6 ppm, $^1J_{Pt-P}$=3893 Hz, $^2J_{P-P}$=43 Hz

δ 25.4 ppm, $^1J_{Pt-P}$=3206 Hz, $^2J_{P-P}$=85 Hz;
δ 28.4 ppm, $^1J_{Pt-P}$=3502 Hz, $^2J_{P-P}$=85 Hz.

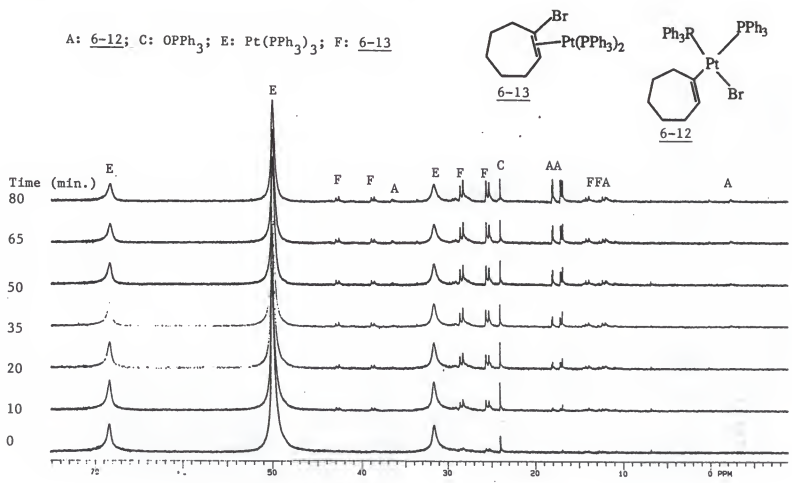
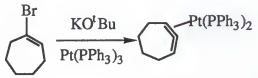


Fig.6-3. A time arrayed ^{31}P NMR of the reaction mixture of 5-5 and $Pt(PPh_3)_3$ in THF solution at -30°C.

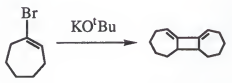
Unfortunately, attempts to isolate this π-complex for reaction with KO^{t}Bu were unsuccessful due to its rapid transformation to 6-12. Direct evidence for the role of 6-13 in the formation of the allene complex 5-1 could therefore not be obtained. In order to obtain indirect evidence, we attempted to compare the rates of the following two reactions (Eq.6-11, and Eq.6-12) using ^{1}H NMR. Unfortunately, at the low temperatures required to retard insertion, $Pt(PPh_3)_3$ precipitates and the undissolved solids reduce the sensitivity and resolution of the ^{1}H NMR experiment to the point that reliable kinetics for Eq.6-11 could not be obtained.

Eq.6-11



5-5 5-1

Eq.6-12



5-5 6-16

Therefore, at this point our mechanistic studies of the reaction in Eq.5-4 have only excluded the insertion mechanism; both the trapping mechanism and the π-complex mechanism remain viable possibilities.

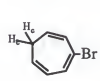
Reaction of Bromocycloheptatrienes (2-1, 2-2 and 2-3) with $Pt(PPh_3)_3$ and KO^tBu

Identification of 2-1, 2-2 and 2-3 from the ^1H NMR Spectrum of a Mixture of Isomers

Bromocycloheptatriene is a mixture of three isomers, 2-1, 2-2 and 2-3. They are difficult to separate and have not previously been individually identified. To study the mechanism of the formation of 1-9 from this mixture, it was first necessary to identify the individual isomers. This was accomplished by synthesizing a mixture of 2-1, 2-2 and 2-3 in which one proton on each side of the bromine atom (in each isomer) has been replaced by a deuterium. These are pictured in $2\text{-}1d_2$, $2\text{-}2d_2$ and $2\text{-}3d_2$.

2-1

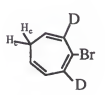
2-2



2-3

$2\text{-}1d_2$

$2\text{-}2d_2$



$2\text{-}3d_2$

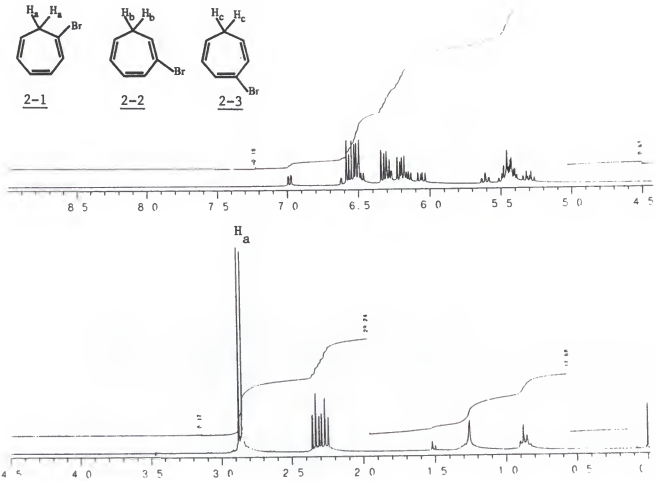


Fig.6-4. The ^1H NMR spectrum of the mixture of 2-1, 2-2 and 2-3.

From the ^1H NMR spectrum of a mixture of 2-1, 2-2 and 2-3 (Fig.6-4), the doublet at 2.85 ppm can be assigned to H_a in 2-1 because H_a only couples to one proton, but H_b and H_c cannot be assigned. However, when Fig.6-4 is compared with the ^1H NMR spectrum of the mixture of 2-1d_2, 2-2d_2 and 2-3d_2 (Fig.6-5), assignments become clear. Thus, the triplet for H_b in **2-2** should become a doublet in 2-2d_2 while H_c in 2-3 should be unaffected. From Fig.6-5, it can be seen that the triplet at 2.26 ppm has symplified to a doublet, which means it must be assigned to 2-2, while the triplet at 2.32 ppm remains almost unchanged, so it must be the H_c of 2-3. As expected, the peak intensity of H_a has decreased one half and H_a is split into a doublet of triplets; the doublet is due to one H-H three-bond coupling while the triplet is due to the H-D two-bond coupling.

Therefore, in the ^1H NMR spectrum of the mixture of 2-1, 2-2 and 2-3 (Fig.6-4), the doublet at 2.85 ppm is from 2-1, the triplet at 2.26 ppm is from 2-2 and the triplet at 2.32 ppm is from 2-3.

Mechanistic Studies

The mechanism of formation of 1-9 (Eq.6-13) was studied by using the same methods that were used to study the formation of 5-1.

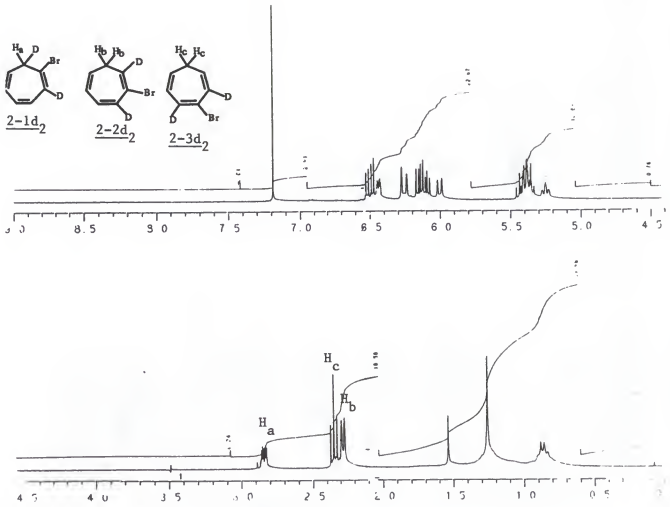
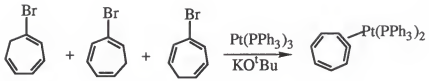


Fig.6-5. The ^1H NMR spectrum of the mixture of 2-1d$_2$, 2-2d$_2$ and 2-3d$_2$.

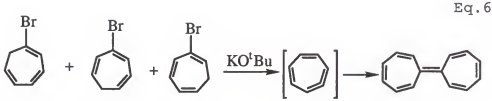
Eq.6-13



2-1 2-2 2-3 1-9

At room temperature, 2-1, 2-2 and 2-3 all react with KO^tBu essentially immediately and the sole product is the dimer, heptafuvalene 6-17. This reaction was carefully studied some time ago and shown to go via the cyclic allene intermediate (Eq.6-14).[62] Under the same conditions but in the presence of $Pt(PPh_3)_3$, allene complex 1-9 was found.

Eq.6-14

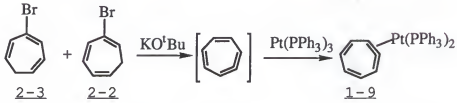


2-1 2-3 2-2 6-17

However, when the mixture of 2-1, 2-2 and 2-3 were treated with $Pt(PPh_3)_3$ in the absence of base at room temperature, the CH_2 peaks of H_b and H_c remained essentially unchanged after 40 minutes while the CH_2 peak of H_a substantially decreased (Fig.6-6). It was later found that no obvious reaction had occurred, even after 2-2 and 2-3 had

been stirred with $Pt(PPh_3)_3$ at 50°C in benzene for 24 hours. Therefore, for 2-2 and 2-3 in Eq.6-13, the reaction mechanism cannot be the insertion mechanism. In view of the rapid reaction in Eq.6-14, the trapping mechanism, shown in Eq.6-15, appears likely even though there is not sufficient information to exclude the π-complex mechanism.

Eq.6-15



2-3 2-2 1-9

In the ^{31}P NMR, it was found that 2-1 reacts with $Pt(PPh_3)_3$ very fast at -30°C to give the cis-insertion complex 6-18. No π-complex, however, was detected by ^{31}P NMR even at -50°C.

The cis-insertion complex 6-18 shows two doublets in the ^{31}P NMR spectrum (CD_2Cl_2, -30°C); 16.3 ppm ($^1J_{Pt-P}$=1569 Hz, $^2J_{P-P}$=14.6 Hz) and 15.8 ppm ($^1J_{Pt-P}$=4580 Hz). The ^{195}Pt NMR of 6-18 gives a doublet of doublets at -4538.7 ppm. All the proton resonances are broad and no coupling constants could be obtained from the ^1H NMR spectrum. It is interesting to note, that, based on integral ratio, the two allylic protons H_a may be nonequivalent: one is at 0.95 ppm, the other may be at 3.16 ppm. The insertion complex 6-18 completely isomerizes to its trans isomer 4-9[21] at room temperature in benzene after 24 hours or one hour at 60°C (Eq.6-16).

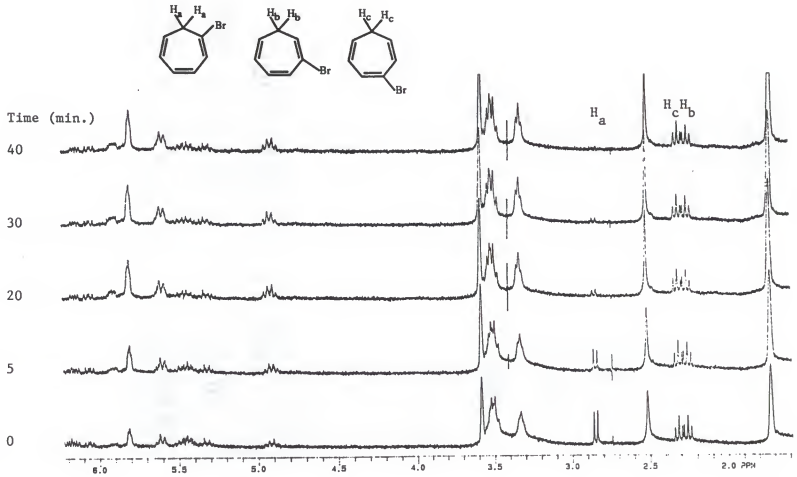
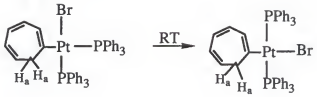


Fig.6-6. A time arrayed ^1H NMR of the reaction mixture of 2-1, 2-2 and 2-3 with $Pt(PPh_3)_3$ at room temperature.

Eq.6-16



6-18 4-9

When 6-18 was isolated and treated with KO^{t}Bu, no allene complex 1-9 could be detected. This result excludes the insertion mechanism for Eq.6-12. However, as in the case of the formation of 5-1, both trapping and π-complex mechanisms are valid possibilities.

CHAPTER 7
SYNTHESIS AND STRUCTURE OF PT(0) COMPLEXES OF CYCLOHEPTADIENYNE 1-13 AND 1-14.

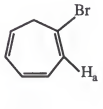
Introduction

In Chapter 5 it was found that the regiochemistry of elimination of HBr from bromocycloheptene in the presence of tris(triphenylphosphine)platinum is highly base dependent; when the elimination is induced by KO^tBu, β-elimination of the sp^3 hydrogen to give an allene complex is the predominant reaction while lithium diisopropylamide (LDA) prefers the vinylic β-hydrogen of either bromocycloheptene or bromocyclohexene, in these cases giving complexes of cyclic alkynes.

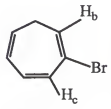
Consistent with the first of the above observations, β-elimination of HBr from a mixture of bromocycloheptatrienes in the presence of bis(triphenylphosphine)platinum using KO^tBu as the base leads to the complex of cycloheptatetraene 1-9 (Chapter 2). In this chapter, the chemistry of the reaction of the mixture of bromocycloheptatrienes with LDA will be explored. This chemistry is of particular interest because, although all three isomeric bromocycloheptatrienes could lead to cyclic alkynes by β-elimination of a vinyl hydrogen, two of the isomers could also give 1,2,3,5-cyclohepatetraene.

Synthesis of 1-13 and 1-14

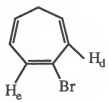
In the three bromocycloheptatetrienes 2-1, 2-2 and 2-3, there are five different vinyl protons (H_a, H_b, H_c, H_d and H_e). All are beta to the bromine. Therefore, β-elimination of HBr with abstraction of a vinyl hydrogen could possibly produce three complexes, 1-13, 1-14 and 7-1. In fact, only a mixture of 1-13 and 1-14 (which are inseparable) were formed when a mixture of bromocycloheptatrienes 2-1, 2-2 and 2-3 was added to a mixture of LDA and $Pt(PPh_3)_3$ at room temperature (Eq.7-1); no trace of 7-1 was detected. This suggests that the LDA can only abstract those vinyl protons which share the same double bond with the bromine (H_a, H_b and H_e).



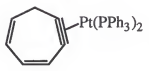
2-1



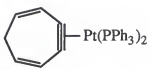
2-2



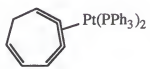
2-3



1-13



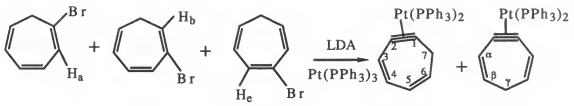
1-14



7-1

The products 1-13 and 1-14 were isolated by adding hexane and purified by recrystallization from THF/hexane solution.

Eq.7-1



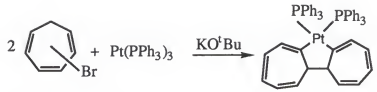
2-1 2-2 2-3 1-13 1-14

2 : 1 : 1 8 : 1

In the mixture of 2-1, 2-2 and 2-3, the ratio of 2-1 : 2-2 : 2-3 is about 2 : 1 : 1 (see Fig.6-4). If all three vinyl protons (H_a, H_b and H_e) have the same reactivity towards LDA, the ratio of 1-13 : 1-14 in the product mixture should be about 3 : 1. The actual ratio, however, is about 8 : 1 based on the proton NMR spectrum.

The synthesis of 1-13 and 1-14 (Eq.7-1) is different in an interesting way from the synthesis of allene complex 1-9 (Eq.2-1). In that case, an excess of bromocycloheptatrienes produces a dimer 7-2 instead of the allene complex 1-9 (Eq.7-2). In Eq.7-1, however, an excess of bromocycloheptatrienes produces no detectable dimers; instead, an excess of the halide is required to optimize the yield of the dienyne complexes. In view of the excess of bromocycloheptatrienes, the observed product ratio for 1-13 and 1-14 of 8 : 1 instead of 3 : 1 suggests that H_e may be less reactive towards LDA than H_a and/or H_b.

Eq.7-2



a mixture of 2-1, 2-2 and 2-3

7-2

NMR Spectroscopy of 1-13 and 1-14

The ^{1}H NMR spectrum of the mixture of 1-13 and 1-14 is showed in Fig.7-1. Based on chemical shifts, coupling patterns and peak intensities, the resonances at 2.42 ppm are assigned to H_γ (see Eq.7-1 for the assignment of the symbols), 6.38 ppm to H_α and 3.32 ppm to H7. The chemical shifts of the remaining protons on the seven-membered-ring of the two products were assigned by COSY (Fig.7-2). The COSY spectrum indicated that H3 is at 5.88 ppm. This proton should couple to the platinum of 1-13 because it is only three-bonds away from the platinum, but in Fig.7-1, the satellite peaks of H3 are not clear. In order to double-check the assignment from the COSY, a Pt-H 2D heteronuclear chemical shift correlation NMR experiment (Fig.7-3) was performed. From Fig.7-3, it is clear that both the H3 and H7 are coupled to the platinum of 1-13 (the doublet of doublets at -4667

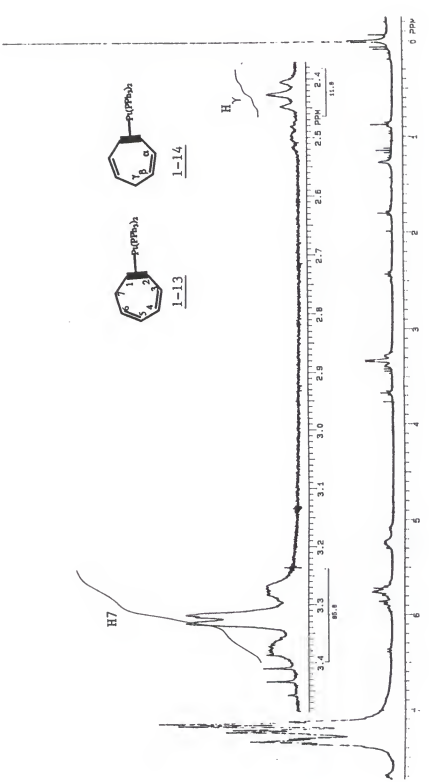


Fig.7-1. The ^{1}H NMR spectrum of the mixture of 1-13 and 1-14.

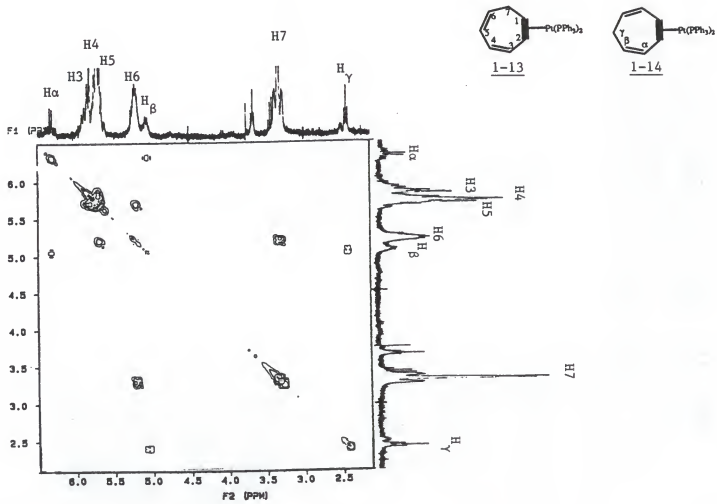


Fig.7-2. The 2D (COSY) NMR spectrum of the mixture of 1-13 and 1-14.

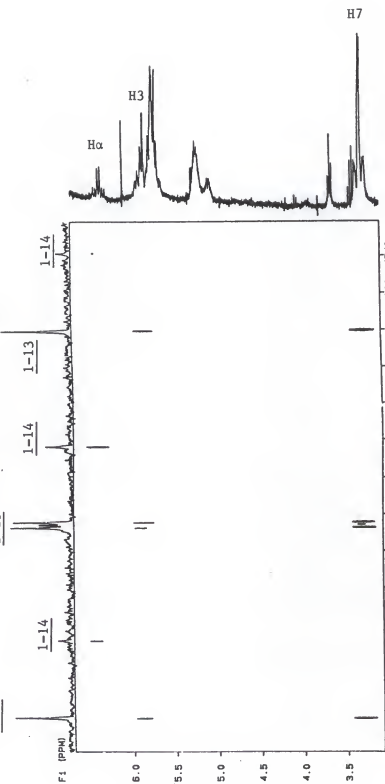


Fig.7-3. The Pt-H 2D (HETCOR) NMR spectrum of the mixture of 1-13 and 1-14.

ppm). Fig.7-3 also confirms that the H_α is coupled to the platinum of 1-14 (triplet at -4689 ppm).

Assignments for the carbon resonances of the seven-membered ring in the ^{13}C NMR were accomplished with the aid of a C-H 2D heteronuclear correlation NMR experiment (Fig.7-4) except for the triple-bond carbons which do not give crosspeaks in the 2D NMR spectrum.

The two phosphorus nuclei in 1-13 are nonequivalent, but their chemical shifts are so close that they appear as a singlet at 28.1 ppm in the ^{31}P NMR spectrum (Fig.7-5). Fortunately, the coupling constants of the two phosphorous atoms to the platinum are slightly different. Therefore, the satellite peaks are not overlapped and show pseudo quartets. These pseudo quartets aided in the identification of complex 1-13.

Crystal Structure of 1-13

The crystal structure is represented in Fig.7-6; important bond lengths and bond angles are listed in Table 7-1. Simply from bond lengths, it is difficult to tell whether the crystal structure is for 1-13 or 1-14. From the bond angles of C(6)-C(7)-C(1) [115.0(2)°] (close to 109°) and C(4)-C(5)-C(6) [131.0(4)°] (close to 120°), however, it is clear that C(7) is an sp^3 carbon and C(5) is an sp^2 carbon. Therefore, this is the crystal structure of 1-13. In order to

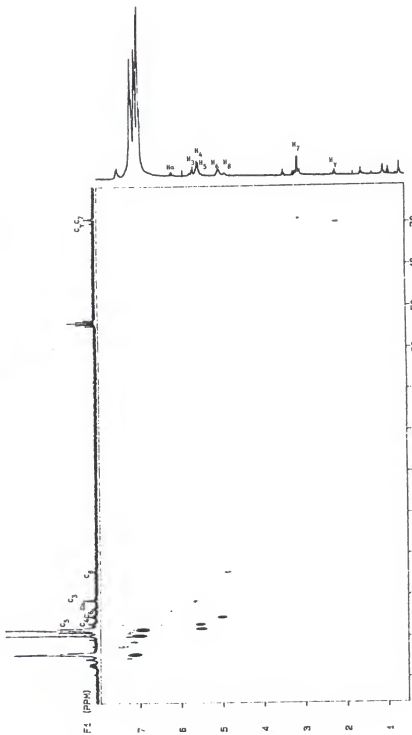


Fig.7-4. The C-H 2D (HETCOR) NMR spectrum of the mixture of 1-13 and 1-14.

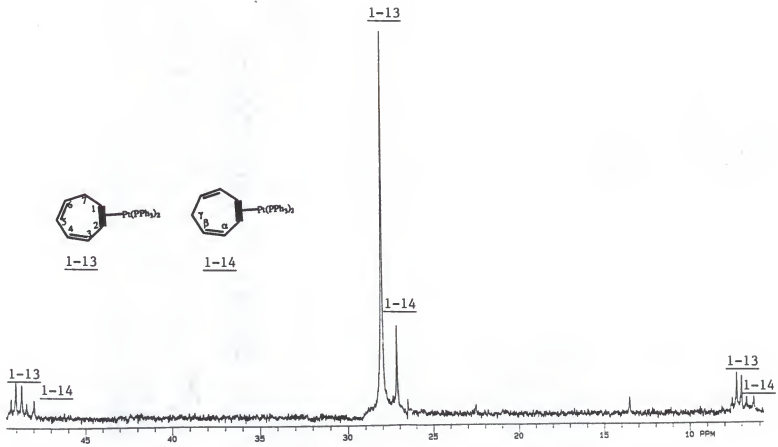


Fig.7-5. The ^{31}P NMR spectrum of the mixture of 1-13 and 1-14.

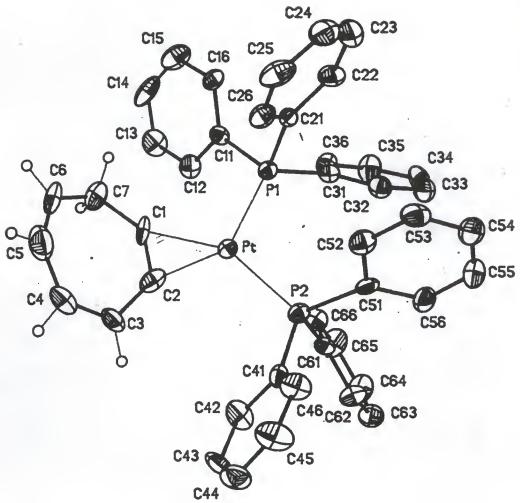


Fig.7-6. Crystal structure of 1-13.

Table 7-1. Bond lengths (Å) and angles (°) for the non-H atoms of compound 1-13.

Pt-P(1)	2.275(4)	Pt-P(2)	2.270(3)
Pt-C(1)	2.058(11)	Pt-C(2)	2.00(2)
C(1)-C(2)	1.31(2)	C(1)-C(7)	1.41(2)
C(2)-C(3)	1.42(3)	C(3)-C(4)	1.31(3)
C(4)-C(5)	1.37(3)	C(5)-C(6)	1.37(4)
C(6)-C(7)	1.38(3)		
P(1)-Pt-P(2)	107.16(12)	P(1)-Pt-C(1)	105.1(5)
P(2)-Pt-C(1)	147.7(5)	P(1)-Pt-C(2)	142.3(4)
P(2)-Pt-C(2)	110.2(4)	C(1)-Pt-C(2)	37.5(6)
Pt-C(1)-C(2)	68.6(9)	Pt-C(1)-C(7)	155.1(14)
C(2)-C(1)-C(7)	136.0(2)	Pt-C(2)-C(1)	73.9(9)
Pt-C(2)-C(3)	157.0(10)	C(1)-C(2)-C(3)	128.3(14)
C(2)-C(3)-C(4)	121.0(2)	C(3)-C(4)-C(5)	129.0(2)
C(4)-C(5)-C(6)	131.0(2)	C(5)-C(6)-C(7)	128.0(2)
C(1)-C(7)-C(6)	115.0(2)		

compare the structural features of complex 1-13 with that of the bis(triphenylphosphine)platinum complex of cycloheptyne 5-8,[63] the bond lengths and bond angles of 1-13 and 5-8 are listed in Table 7-2 and Table 7-3, respectively. Within the

experiment error, the triple bond in 1-13 is equal to that in 5-8. For the rest of the bonds, however, the bond lengths in 1-13 are, on average, shorter than in 5-8 and the bond angles of 1-13 are, on average, larger than the bond angles of 5-8. These are consistent with the fact that the dienyne C_7H_6 has more double bonds (which are shorter than single bonds) and more sp^2 carbons (which have larger bond angle than sp^3 carbons) in the ring than cycloheptyne.

Table 7-2. Comparison of bond lengths in 1-13 with those in 5-8.

Bond	1-13	5-8
C(1)-C(2)	1.31(2)	1.283(5)
C(2)-C(3)	1.42(3)	1.485(6)
C(3)-C(4)	1.31(3)	1.536(7)
C(4)-C(5)	1.37(3)	1.448(8)
C(5)-C(6)	1.37(4)	1.445(9)
C(6)-C(7)	1.38(3)	1.492(7)
C(1)-C(7)	1.41(2)	1.476(6)

Table 7-3. Comparison of bond angles (°) in 1-13 with those in 5-8.

Angle	1-13	5-8
C(2)-C(1)-C(7)	136.0(2)	141.4(4)
C(1)-C(7)-C(6)	115.0(2)	112.3(4)
C(7)-C(6)-C(5)	128.0(2)	121.0(5)
C(6)-C(5)-C(4)	131.0(2)	125.5(5)
C(5)-C(4)-C(3)	129.0(2)	122.0(5)
C(4)-C(3)-C(2)	121.0(2)	111.4(4)
C(1)-C(2)-C(3)	128.3(14)	136.4(4)

Within experiment error, the triple-bond bond lengths of the $Pt(PPh_3)_2$ complex of cycloheptadienyne 1-13 [1.31(2)Å], cyclohexyne 5-7 [1.297(8)Å][63] and cycloheptyne 5-8 [1.283(5)Å] are equal. The IR stretching frequencies, however, are quite different. From 5-8 to 5-7, the frequency decreases from 1770 cm^{-1} to 1721 cm^{-1}. This has been explained as resulting from greater strain in 5-7 which leads to greater back-bonding donation of electrons from the central metal of the cycloalkyne complex into the antibonding alkyne orbital which increases the triple bond length and lowers its IR stretching

frequency.[63] From 5-8 to 1-13 the triple bond stretching frequency also decreases significantly from 1770 cm^{-1} to 1712 cm^{-1}. This is possibly due primarily to conjugation with the additional double bonds,[64] although it is possible that 1-13 is also more strained than 5-8.

A Summary of Dehydrobromination of Bromocycloalkene

A comparison of LDA with KO^tBu and their application in dehydrobromination are summarized in Fig.7-7. The results in this chapter further confirm that LDA exclusively removes vinylic protons which share the same double bond with the bromine.

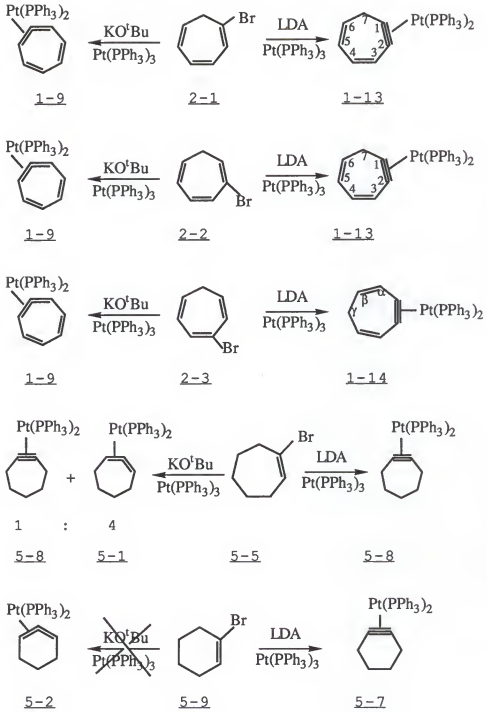
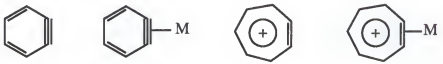


Fig.7-7. A summary of the application of LDA and KO^{t}Bu.

CHAPTER 8
SYNTHESIS OF A PLATINUM(0) TROPYNE COMPLEX

Introduction

Extensive research has been carried out on benzyne 8-1 and its transition metal complexes 8-2[65-67] and two good reviews on metal benzyne complexes have recently been published.[9,68] In contrast, the tropylium analogue of benzyne 8-3 (for the sake of brevity, it will be referred to as tropyne), to our knowledge, has not been reported either as a reactive intermediate or as its metal complexes 8-4.



8-1 8-2 8-3 8-4

Tropyne, is intriguing to us for three reasons.

First, molecular mechanics calculations (the MMX program)[69] predict that it should be a highly strained molecule (somewhat less than benzyne) and some of the chemistry of its metal complexes should be quite interesting.

Second, both tropyne complex 8-4 and cycloheptatrienylidene (carbene) complex 8-5 (see Fig.8-1) are formed by the interaction of an organic fragment with a

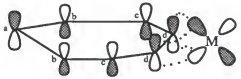
metal fragment, and, although these interactions are different, they have interesting similarities. Fig.8-1 compares the σ-bonding and π-back bonding of the tropyne complex 8-4 with those of the carbene complex 8-5. The σ-bonding in 8-4

8-4

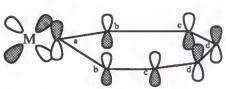
8-5

(a) σ-bonding of 8-4.

(b) σ-bonding of 8-5.



(c) π-back bonding of 8-4.



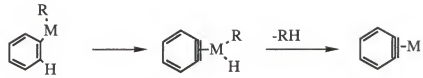
(d) π-back bonding of 8-5.

Fig.8-1. Orbital pictures of the σ-bonding and π-back bonding of tropyne complex and those of carbene complex.

is formed by the interaction between the HOMO of the tropyne fragment with the LUMO d orbital of the metal [Fig.8-1(a)]. Similarly, in carbene complex 8-5 the σ-bond is formed by the interaction between the HOMO of the cycloheptatrienylidene (essentially an sp^2 orbital) and the LUMO d orbital of the metal as pictured in Fig.8-1(b). The π-back bonding of 8-4 is also similar to 8-5. The conjugated tropylium ion π-system has two degenerate LUMO orbitals.[54] Only one has a symmetry that permits it to interact with the HOMO d orbital of the metal [see Fig.8-1(c) and (d)]. In tropyne complex 8-4, the HOMO d orbital of the metal mixes with the LUMO bisecting two $C_{(d)}$ carbons [Fig.8-1(c)]; in carbene complex 8-5, the HOMO d orbital of the metal mixes with the same LUMO at $C_{(a)}$ carbon [Fig.8-1(d)]. These bonding features should lead to interesting physical and chemical properties of the tropyne complex 8-4 and the carbene complex 8-5.

And finally, the most common method to prepare benzyne complexes is β-hydride elimination of a phenyl complex 8-6 followed by a reductive elimination of RH (Eq.8-1 or its equivalent).[70-77] It would be interesting to determine if the same methodology could be applied to the synthesis of tropyne complexes although we know of no confirmed cases of β-hydride elimination from a carbene complex. Carbene complex 8-5 can also be represented as a tropylium ion complex 8-7 in which such a reaction might occur. It would therefore be interesting to see if the reaction in Eq.8-2 could take place.

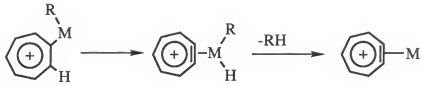
Eq.8-1



8-6 8-2

8-5 8-7

Eq.8-2



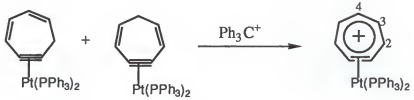
8-4

In this Chapter, synthesis of the first tropyne complex will be reported and its spectrum and bonding will be discussed. Reactions of tropyne complexe and other methods of its synthesis mentioned above will be the subject of future research.

Synthesis and Spectroscopy of 1-15

Complex 1-15 was synthesized by hydride abstraction from 1-13 and 1-14 (see Chapter 7) with $Ph_3C^+BF_4^-$ in methylene chloride solution at -78°C (Eq.8-3). The product was then precipitated as its BF_4^- salt by adding an excess of ether.

Eq.8-3



1-13 1-14 1-15

The tropyne complex 1-15 was characterized by ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR, NOE, 2D COSY, and 2D C-H HETCOR NMR. All of the proton resonances on the tropyne ring (Fig.8-2) are shifted downfield compared to those of 1-13 and 1-14 but upfield compared to 9.55 ppm of tropylium ion.[78,79] Among H2, H3 and H4, H2 is at the highest field (7.66 ppm, $^3J_{Pt-H}$=51.9 Hz) and H4 is in the lowest field (8.64 ppm, $^3J_{H-H}$=10.0 Hz).

In the ^{13}C NMR spectrum (Fig.8-3), all carbon nuclei in the tropyne ring are shifted downfield compared to those of 1-13 and 1-14, but upfield when compared to those in the tropylium ion (160.6 ppm).[78,79] Among C2, C3 and C4, C2 is at the highest field (135.6 ppm) but C3 (150.0 ppm $^3J_{Pt-C}$=53.2

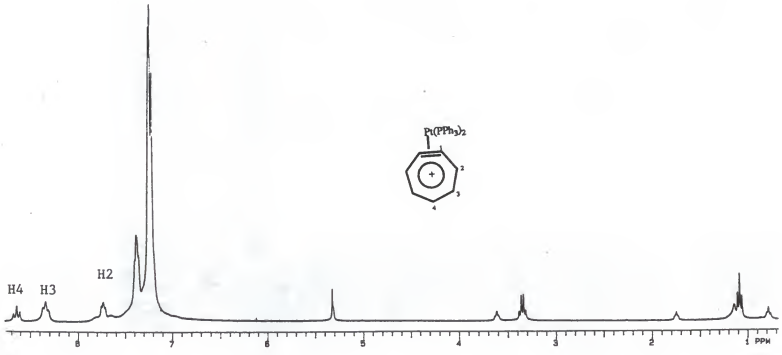


Fig.8-2. The ^{1}H NMR spectrum of 1-15.

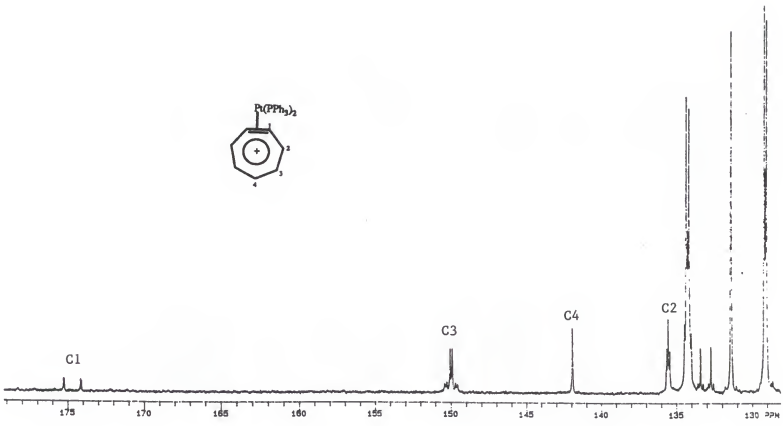
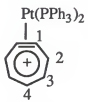


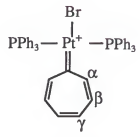
Fig.8-3. The ^{13}C NMR spectrum of 1-15.

Hz, $^4J_{P-C}$=10.5 Hz), instead of C4 (141.8 ppm), is at the lowest field. This trend is different from that observed in the proton NMR spectrum.

A comparison of the carbon NMR data in the seven-membered ring of the carbene complex 1-12 with the tropyne



1-15



1-12

complex 1-15 is very enlightening. The σ-bonding interaction to which both the carbene carbon (C_{carb}) in 1-12 and the triple bond carbon (C1) in 1-15 are subjected will complicate the comparison, therefore only the C_α (162.5 ppm), $C\beta$ (143.5 ppm) and C_γ (146.5 ppm) in 1-12, and the C2 (135.6 ppm), C3 (150.0 ppm) and C4 (141.8 ppm) in 1-15 will be compared. In other words only the remote effect of π-back bonding on the seven-membered ring system will be considered here. First, in an overall comparison, the average chemical shift of these three carbons is 150.8 ppm in 1-12 and 142.5 ppm in 1-15 which indicates that the seven-membered ring in the tropyne complex 1-15 has, on average, higher electron density than in the carbene complex 1-12. This may further suggest that the LUMO of the seven-membered ring in 1-15 receives more

electron density from the HOMO of the platinum than the LUMO in 1-12 does. This, however, could also be an inductive effect.

When the chemical shifts of $C\alpha$ (162.5 ppm), $C\beta$ (143.5 ppm) and $C\gamma$ (146.5 ppm) of 1-12 are compared, they show that $C\alpha$ is significantly downfield from $C\beta$ and $C\gamma$. The same trend has been found for all carbene complexes listed in Table 4-2 (page 49). A comparison of C2 (135.6 ppm), C3 (150.0 ppm) and C4 (141.8 ppm) of 1-15 shows that C3 is furthest downfield. From Fig.8-1c and Fig.8-1d, it is clear that both the $C\alpha$ of 1-12 and the C3 of 1-15 are actually the same carbon [$C_{(b)}$] of the tropylium ion fragment(see Fig.8-4). As mentioned in

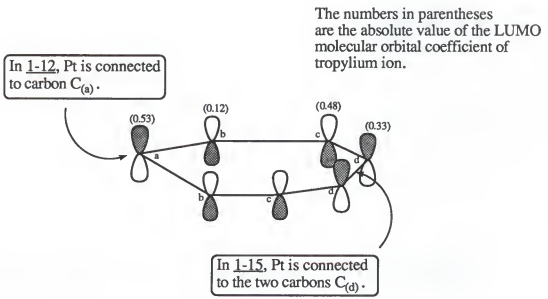
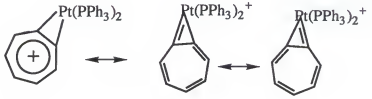


Fig.8-4. Metal Pt atacks from different side of the LUMO of tropylium ion.

Chapter 4, according to simple Huckel molecular orbital calculation, the orbital coefficient of $C_{(b)}$ of the LUMO of the tropylium ion has the smallest absolute value (0.12).[54] The ^{13}C NMR results for 1-12 and 1-15 indicate that no matter whether the platinum is connected to one carbon $C_{(a)}$ or to two carbons $C_{(d)}$, the chemical shift of carbon $C_{(b)}$ is always furthest downfield. This is consistent with the calculations. That is, if electron density is distributed in the LUMO of a tropylium ion (here, this electron density comes from the π-back bonding of the metal), $C_{(b)}$ receives the least amount of the electron density. It is important to note, however, that other different transition metal tropyne complexes are needed to support this suggestion.

The $^1J_{Pt-C}$ constants of Pt(0) complexes of cyclic alkynes 5-8 (318 Hz), 5-7 (395 Hz) and 6-7 (436 Hz) increase with decreasing ring size, yet the $^1J_{Pt-C}$ constant in 1-15 ($^1J_{Pt-C}$=458.5 Hz) is larger than that of even the most strained. According to Bennett, this trend in the metal complexes suggests that the σ bonding orbital used in the alkyne-Pt bond contains a large amount of 6 s-character,[9] leading to relatively strong bonding between the alkyne and the platinum. However, in a discussion of the relationship between phosphorus-tungsten coupling constants and s-character in their bonding, Buhro, Chisholm et al.[80] point out that "for a given atom Z, variation in P-Z coupling appears to be dominated by variation of the s-electron density brought about by changes in hybridization at phosphorus." At

this time we think the suggestion of Buhro, Chisholm et al. is more credible. Buhro, Chisholm et al. also suggest that the s-character of phosphorus in a P-W bond has a deshielding effect. Therefore, increasing the s-character will result in a chemical shift of phosphorus to downfield and an increased P-W coupling constant. If this is also correct for platinum-carbon bonds, increasing the s-character could contribute to the lower-field chemical shift (174.6 ppm) of C1. Perhaps more importantly, the large $^{1}J_{Pt-C}$ coupling constant (458.5 Hz) in 1-15 (even larger than the cyclopentyne complex) suggests that the the coordination bonding between Pt and the triple bond in 1-15 contains more carbon s-character than it does in simple cyclic alkyne Pt(0) complexes 5-8, 5-7 and 6-7. Thus tropyne complex 1-15 may have significant contribution from metallocyclpropene complex 8-8. The $^{1}J_{Pt-C}$ coupling constant should also be increased by contributions of resonance structures such as 8-9 and 8-10. Complexes with Pt=C character are known to have large $^{1}J_{Pt-C}$ coupling constant.[55]



8-8 8-9 8-10

In the tropyne fragment of 1-15 as in the carbene fragment of the Pt(II) carbene complex 1-12, the three bond coupling constant between Pt and C ($^3J_{Pt-C}$=53.2Hz) is larger than the two bond coupling, which is too small to be detected. This is common in complexes of Pt(II) with saturated hydrocarbon ligands,[81] but in the case of Pt(0) complexes, this phenomenon is not well documented.

The chemical shifts in the ^{31}P NMR spectrum showed little change when 1-13 (28.0 ppm $^1J_{Pt-P1}$=3370.2 Hz, $^1J_{Pt-P2}$=3404.4 Hz) and 1-14 (27.2 ppm $^1J_{Pt-P}$=3392.4 Hz) were converted to 1-15 (21.5 ppm $^1J_{Pt-P}$=3121.8 Hz) but in the ^{195}Pt NMR spectrum, the chemical shift of 1-15 (-3788 ppm) is not only significantly downfield from 1-13 (-4668 ppm) or from 1-14 (-4686 ppm), but also downfield from the Pt(II) carbene complex 1-12 (-4095 ppm). Even taking into account resonance structures such as 8-9 and 8-10 in which the platinum is formally Pt(II), the chemical shift difference between 1-15 (-3788 ppm) and 1-12 (-4095 ppm) is still significant. According to the orbital interactions pictured in Fig.8-1, this is consistent with greater π-back bonding from the HOMO d orbital of the platinum into the LUMO of the tropylium ion ring in 1-15 than in 1-12. This is also consistent with the conclusions reached from the ^{13}C NMR data of 1-15. We must be aware, however, that chemical shifts of Pt are affected by many factors.[82] It is possible that other factors may be the principal cause of the downfield shift in the ^{195}Pt NMR spectrum of 1-15 downfield.

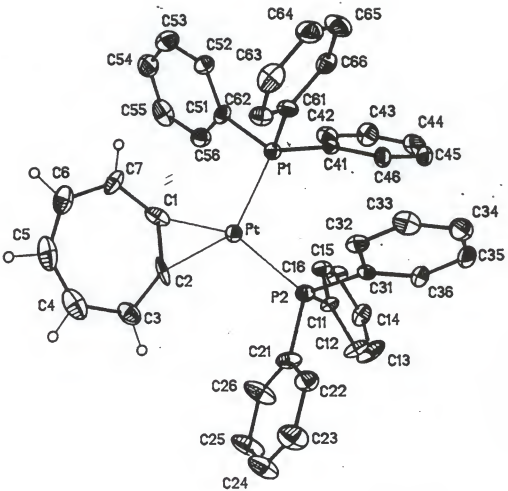


Fig.8-5. Crystal structure of 1-15.

Table 8-1. Bond lengths (Å) and angles (°) for the non-H atoms of compound 1-15.

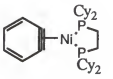
Pt-P(1)	2.316(4)	Pt-P(2)	2.310(4)
Pt-C(1)	2.00(2)	Pt-C(2)	2.044(13)
C(1)-C(2)	1.37(2)	C(1)-C(7)	1.39(2)
C(2)-C(3)	1.35(2)	C(3)-C(4)	1.41(3)
C(4)-C(5)	1.40(3)	C(5)-C(6)	1.39(3)
C(6)-C(7)	1.37(2)		
P(1)-Pt-P(2)	104.20(13)	P(1)-Pt-C(1)	103.5(4)
P(2)-Pt-C(1)	152.0(4)	P(1)-Pt-C(2)	143.0(5)
P(2)-Pt-C(2)	112.6(5)	C(1)-Pt-C(2)	39.5(6)
Pt-C(1)-C(2)	71.9(8)	Pt-C(1)-C(7)	154.8(12)
C(2)-C(1)-C(7)	132.7(14)	Pt-C(2)-C(1)	68.6(9)
Pt-C(2)-C(3)	156.1(13)	C(1)-C(2)-C(3)	135.1(14)
C(2)-C(3)-C(4)	120.0(2)	C(3)-C(4)-C(5)	128.0(2)
C(4)-C(5)-C(6)	1135.0(2)	C(5)-C(6)-C(7)	127.0(2)
C(1)-C(7)-C(6)	122.7(15)		

The crystal structure of 1-15 is represented in Fig.8-4. The important bond lengths and bond angles are listed in Table 8-1. The seven-membered ring in Fig.8-4 is flat and the platinum atom is almost in the same plane of the seven-membered ring (the angle between the tropyne ring and the plane of $Pt-C_1-C_2$ is 4°).

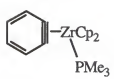
Table 8-2 compares the C-C bond lengths in benzyne complexes 8-11 and 8-12[9] with those in tropyne complex 1-15.

Table 8-2. Comparison of C-C bond lengths (Å) in benzyne complexes 8-11 and 8-12 with those in tropyne complex 1-15.

Bond	1-15	8-11	8-12
C(1)-C(2)	1.37(2)	1.332(6)	1.364(8)
C(2)-C(3)	1.35(2)	1.386(6)	1.389(8)
C(3)-C(4)	1.41(3)	1.383(7)	1.383(9)
C(4)-C(5)	1.40(3)	1.390(8)	1.380(9)
C(5)-C(6)	1.39(3)	1.383(7)	1.377(9)
C(6)-C(7)	1.37(2)		
C(1)-C(7)	1.39(2)		
C(6)-C(1)		1.389(6)	1.406(8)



8-11



8-12

The triple bond in a benzyne complex is usually lengthened compared to the value of 1.29 Å found for most ML_2(alkyne) (M=Pt, Ni) and $ZrCp_2(PMe_3)$(alkyne) complexes. Correspondingly, the stretching frequencies of the benzyne triple bond are around 1580 cm^{-1}, which are less than the value of ca. 1700 cm^{-1} found in simple alkyne complexes.[9] The tropyne complex 1-15 shows similar trends. The triple bond of 1-15 is 1.37(2) Å, which is significantly longer than 1.29 Å; the stretching frequency of the triple bond in 1-15 is 1634 cm^{-1}, which is less than the value of 1712 cm^{-1} for the complex 1-13. Note that the stretching frequency of the tropyne triple bond in 1-15 (1634 cm^{-1}) is greater than is typical of benzyne complexes. This suggests that the triple bond in the tropyne complex is less perturbed than the one in benzyne complexes and the tropyne complex may be less strained than its benzyne counterpart.

Comparing bond lengths in the rings, it is found that in tropyne complex 1-15, all bonds in the tropyne ring are nearly equal within experimental error. Similarly, in benzyne complexes 8-11 and 8-12, all bonds in the ring are nearly equal except for the triple bonds [C(1)-C(2)], which are a little shorter than the rest of the bonds.[73,74]

In complexes 1-13 and 1-15, the bond distances of the Pt-C bonds do not differ significantly. The Pt-P bond distance in 1-15 [2.316(4)Å and 2.310(4)Å], however, is significantly longer than that of 1-13 [2.275(4)Å and 2.270(3)Å]. The longer bond lengths of 1-15 correlate well with the smaller $^{1}J_{Pt-P}$ constants of 1-15 (3121.8 Hz) in comparison with the $^{1}J_{Pt-P}$ constants of 1-13 which are 3370.2 Hz and 3404.4 Hz.

Table 8-3 lists the ^{195}Pt NMR chemical shifts and the $^{1}J_{Pt-P}$ coupling constants of the cyclic allene and cyclic

Table 8-3. A list of the ^{195}Pt NMR chemical shifts and $^{1}J_{Pt-P}$ constants of cyclic allene and cyclic alkyne Pt(0) complexes.

Complexes	δ of ^{195}Pt NMR	$^{1}J_{Pt-P}$ constants
1-9	-4646	3170.1, 3266.7
1-13	-4667	3370.2, 3404.4
1-14	-4689	3392.4
1-15	-3788	3221.8
5-1	-4939	3135.4, 3171.2
5-8	-4698	3427.9
5-7	-4658	3388.0

alkyne Pt(0) complexes. Among the complexes of 1-9, 1-13, 1-14, 5-7 and 5-8, the δ values in the ^{195}Pt NMR spectrum do not show significant differences, while the δ value of 5-1 is more than two hundred ppm upfield from the other complexes.

Except for 1-15, $^{1}J_{Pt-P}$ is smaller for allene structures than for alkyne structures. The bond distances between Pt and P are 2.287(2)Å and 2.299(2)Å in 1-9 (see Table 2-1) which are longer than the Pt-P bond distances, 2.275(4)Å and 2.270(3)Å, in 1-13 (see Table 7-1). These results suggest that the Pt-P bonding in allene complexes may be weaker than in alkyne complexes.

CHAPTER 9
EXPERIMENTAL

Equipment

The NMR spectra were recorded on a Varian VXR-300, or General Electric QE-300, or Varian XL-200 with TMS as the reference for ^{1}H and ^{13}C NMR; 80% H_3PO_4 as the reference for ^{31}P NMR; toluene-d_8 as the reference for ^{2}H NMR and a saturated solution of K_2PtCl_6 in D_2O as the reference for ^{195}Pt NMR. The IR spectra were obtained from KBr pellets using a PERKIN ELMER 1600 FTIR. The Mass spectra were done by Finnigan Mat 95Q. The X-ray data were collected on a Siemens P3m/v diffractometer equipped with a graphite monochromator. Elemental analysis were performed with a Carlo Erba 1106 Elemental Analysizer.

Materials

THF and ether were purified and rendered oxygen-free by distillation under nitrogen atmosphere with sodium/benzophenone. Hexane was dried by molecular sieves of type 4A and degassed by blowing nitrogen gas through it for 5 hours. Methylene chloride was distilled over P_2O_5. Potassium *tert*-butoxide, triphenylcarbenium tetrafluoroborate, lithium diisopropylamide (LDA) and most of other reagents including

NMR solvents were obtained from Aldrich and used without further purification. 6-Hydroxytropinone was bought from Aldrich and sublimed before use. 2,4,6-Cycloheptatrienone,[83] the mixture of 1-bromo, 2-bromo and 3-bromocyclohepta-1,3,5-triene 2-1, 2-2 and 2-3,[84] tetrakis and tris(triphenylphosphine)platinum(0),[85] 7, 7-dibromobicyclo(4,1,0)heptane 5-3,[86] ethylenebis(triphenylphosphine)platinum(0) 5-4,[87] 1-bromocycloheptene 5-5,[21] 1-bromocyclohexene 5-9,[88] trans-(bromo)(1-η^1-cycloheptenyl)bis(triphenylphosphine)platinum 6-14,[21] and trans-(bromo)(η^1-cyclohepta-1,3,5-trienyl)bis(triphenylphosphine)platinum 4-9[21] were prepared according to the literature procedure.

Spin Saturation Transfer

The NMR sample was prepared as a toluene-d_8 solution (~20mg/0.5ml) in a 5mm NMR tube and degassed by freeze/pump/thaw procedures and sealed on a nitrogen line. Variable-temperature ^1H NMR spectra were collected on a VXR-300 NMR spectrometer. Saturation transfer experiments were performed by inverting (180^o selective pulse) the resonance peaks of H2 (3.41ppm), followed by a variable length of time τ (see Fig.3-3), a 90^o observation pulse, a free induction decay(FID) of 1.872 sec., and a prepulse relaxation delay (D1) of 10 sec. (about 3 to 5 times T_1). Each spectrum consisted of 32 pulse sequences. The data for calculation were collected for the resonances H2 and H7. The absolute

peak intensities were determined by measuring the integral of H2 and H7.

In the study of the fluxional mechanism, the pulse sequence is a typical NOE sequence.

Mechanistic Studies on the Reaction of Bromocycloalkenes with KO^tBu and $Pt(PPh_3)_3$

Solid $Pt(PPh_3)$ and KO^tBu were weighed and transferred to a 5 mm NMR tube. To each sample tube was added 0.5 ml of THF-d_8. The tube was sealed with a rubber septum, flushed with nitrogen gas and cooled to -78°C. When the reaction was monitored at low temperature, the probe in the NMR equipment was first cooled to the required temperature. Bromocycloalkenes (5-5, or the mixture of 2-1, 2-2 and 2-3) were dissolved in 0.2 ml of THF-d_8 and added to the sample tubes with a syringe. The sample tube was then shaken quickly to mix the reagents and put into the NMR probe. The pulse sequences were the normal ^1H or ^{31}P NMR pulse sequences except that there was a set of preacquisition delays so that the acquisition would start automatically after every delay.

Preparation of (1,2-η^2-Cycloheptatetraene)bis(triphenylphosphine)platinum 1-9

The steps reported here are similar to those used by Winchester[21] except for final workup procedures. Thus, potassium t-butoxide (100 mg, 0.89 mmol) and tris(triphenylphosphine)platinum (500 mg, 0.51 mmol) were

weighed into an oven dried Schlenk tube containing a magnetic stirrer. After adding an amount of THF which just dissolved all the solids, the Schlenk tube was sealed with a rubber septum and removed from the drybox. Outside the drybox, a mixture of bromocycloheptatrienes (100 mg, 0.59 mmol) was weighed into a vial and 2 ml of THF added. This solution was drawn into a syringe and added very slowly to the solution in the Schlenk tube over about 30 minutes. During this period, the color of the solution in the Schlenk tube changed from clear orange to turbid yellow or light brown. After about two hours the solution was filtered through celite and 20 ml of hexane was added to the filtrate, forming a turbid solution. This solution cleared and within about two hours small crystals and solids appeared on the wall of flask. The solution was decanted gently and the remaining crystals and solids were recrystallized from THF/hexane. The resulting product showed physical and spectroscopic properties identical to those previously reported.[21]

Preparation of 2,4,6-Cycloheptatienone-2,7-d_2 2-4

6-Hydroxytropinone(1 g, 6.44 mmol) and potassium carbonate (anhydrous) (0.5 g) were dissolved in 15 ml of D_2O at room temperature. After 24 hours, the ^1H NMR showed that deuterium exchange was complete. The D_2O solvent was removed in vacuo and the solids were treated with 20 ml of ethanol. The K_2CO_3 would not dissolve in ethanol while hydroxytropinone would. The solution was filtered and the

filtrate was concentrated to 5 ml *in vacuo* and then cooled with ice. To this solution was added cold methyl iodide(3 g). The reaction mixture was cooled at 5°C for 15 hr at which time the mixture had deposited colorless crystals of the desired salt. After isolation of the crystals by filtration, they were dissolved in 10 ml D_2O containing 0.4 g sodium carbonate. The solution was warmed at 60°C overnight. The ^1H NMR spectrum of the solution showed no changes. The reaction mixture was extracted five times with methylene chloride (10 ml each time). The methylene chloride solution was dried over magnesium sulfate overnight and filtered. After removing the methylene chloride *in vacuo*, the residue was distilled to give 2-4 (0.38g, 54.5%). ^1H NMR (300MHz, $CDCl_3$), δ 6.18-6.26(m, 2H), 6.33-6.42(m,2H); two protonated residue peaks at δ 6.86 and 6.90. ^{13}C NMR (75MHz, $CDCl_3$), δ 127.5(t, $^1J_{D-C}$=25 Hz), 133(s) and 135(s).

Preparation of a Mixture of 1-Bromo-2,7-d_2-, 2-Bromo-1,3-d_2- and 3-Bromo-2,4-d_2-cyclohepta-1,3,5-triene 2-1d_2, 2-2d_2 and 2-3d_2[84]

^1H NMR (300MHz, $CDCl_3$), (Fig.6-5), δ 2.26 (CH_2, d, $^3J_{H-H}$=7 Hz), (2-2d_2), 2.32(CH_2, t, $^3J_{H-H}$=7 Hz), (2-3d_2), 2.85 (CHD, dt, $^3J_{H-H}$=7 Hz, $^2J_{H-D}$=2 Hz), (2-1d_2), vinyl protons: 5.21-5.46(m), 5.97-6.29(m), 6.41-6.54(m).

Preparation of (1,2-η^2-Cycloheptatetraene-2,7-d_2)bis(triphenylphosphine)platinum (1-9d_2)

See preparation of 1-9. ^{1}H NMR (200MHz, toluene- d_8), (Fig.2-5), multiple peaks appear at δ 4.97, 5.87, 6.19, 6.54, 7.00 and 7.45. ^{2}H NMR (46MHz, toluene-d_8), (Fig.2-6), broad peaks at δ 3.41 and 6.16ppm.

Preparation of (1,2-η^2-Cycloheptadiene)bis(triphenylphosphine)platinum 5-1

Visser[6] reported 5-1 but gave no experimental details. We used the following procedures to prepare 5-1. Thus, 0.5 g(0.51 mmole) of tris(triphenylphosphine)platinum and 0.11g (1 mmole) of KO^{t}Bu were dissolved in 10 ml of THF. To this solution was added 0.1g (0.57 mmole) of 1-bromocycloheptene 5-5 in 2 ml of THF dropwise at room temperature. After the solution was stirred for 2 hr, the mixture was filtered through silica gel. The product, 5-1, was precipitated by adding excess hexane. The product was further purified by recrystallization from THF/hexane. Yield: 0.29 g(70%). The ^{1}H NMR chemical shifts are the same as those reported by Visser. Additional NMR data: ^{31}P NMR(121MHz, toluene-d_8) δ 30.6 (d, $^1J_{Pt-P}$=3135 Hz, $^2J_{P-P}$=35 Hz), 34.5(d, $^1J_{Pt-P}$=3171 Hz, $^2J_{P-P}$=35 Hz), ^{195}Pt NMR(64MHz, toluene-d_8) δ -4939(dd, $^1J_{Pt-P_1}$=3137 Hz, $^1J_{Pt-P_2}$=3170 Hz).

Preparation of (1, 2-η^2-cycloheptyne)bis(triphenylphosphine) platinum 5-8

Bennett[57,58] has prepared 5-8 and 5-7 [(1, 2-η^2-cyclohexyne)bis(triphenylphosphine) platinum] by reducing 1, 2-dibromocycloheptene and 1, 2-dibromocyclohexene, respectively, with sodium amalgam in the presence of tris(triphenylphosphine)platinum. We used the following procedure to prepare 5-8. Thus, 0.5 g(0.51 mmole) of tris(triphenylphosphine)platinum and 0.1g (1 mmole) of LDA were dissolved in 10 ml of THF. To this solution was added 0.1g (0.57 mmole) of 1-bromocycloheptene 5-5 in 2 ml of THF dropwise at room temperature. After two hours, the solution was filtered through silica gel. The product, 5-8, was collected by adding excess hexane to induce precipitation. The product was further purified by recrystallization from THF/hexane. Yield: 0.34g (82%). The ^{1}H NMR chemical shift are the same as those reported by Bennett. Additional NMR data: ^{195}Pt NMR (64MHz, toluene-d_8) δ -4698 (t, $^1J_{Pt-P}$=3435 Hz).

Preparation of (1, 2-η^2-cyclohexyne)bis(triphenylphosphine) platinum 5-7

The procedure was same as that described above. Additional NMR data are: ^{195}Pt NMR (64MHz, toluene-d_8) δ -4658 (t, $^1J_{Pt-P}$=3388 Hz).

Preparation of *cis*-(Bromo)(1-η^1-cycloheptenyl)bis(triphenylphosphine)platinum 6-12

Tris(triphenylphosphine)platinum (0.25g, 0.25 mmole) was dissolved in 5 ml of THF. To this solution was quickly added 0.1g (0.57 M mole) of 1-bromocycloheptene (5-5) in 2 ml of THF. After this mixture was stirred 10 min at room temperature, excess hexane was added until a precipitate was formed. The product 6-12 was collected by carefully decanting the supernatant solution, washing the precipitate with hexane and drying on a vacuum line. Yield: 0.14g (63%); Mp 215°C dec; IR 3055w, 2908m, 2847w, 1480m, 1435s, 1400w, 1185w, 1095s, 1028w, 999w,742s, 693vs, 544m, 522vs; ^{1}HNMR(300 MHz, CD_2Cl_2, -20°C, δ) 7.1-1.8(aromatics, 30H), 5.62(br, 1H), 2.58(br, 1H), 1-2(br, 9H); ^{13}C NMR (The fast isomerization of 6-12 to its trans isomer prevented us from obtaining peak assignments); ^{31}P NMR(121 MHz, C_6D_6) δ 17.7 (td, $^1J_{Pt-P}$=4742 Hz, $^2J_{P-P}$=13 Hz), 18.6(td, $^1J_{Pt-P}$=1458 Hz, $^2J_{P-P}$=13 Hz), ^{195}Pt NMR(64MHz, C_6D_6) δ -4567.6(dd, $^1J_{Pt-P_1}$=1458 Hz, $^1J_{Pt-P_2}$=4751 Hz). Anal. calcd. for $C_{43}H_{41}P_2Pt$: C, 57.72; H, 4.62. Found: C, 58.64; H, 4.51.

Preparation of *cis*-(Bromo)(1-η^1-cyclohepta-1, 3, 5-trienyl)bis (triphenylphoshine)platinum 6-18

The procedure used for 6-12 was followed using bromocycloheptatrienes (a mixture of 2-1, 2-2, and 2-3), instead of 5-5. Yield: 64%; Mp 168°C dec; IR 3055w, 2907m, 2847w, 1480m, 1435s, 1185w, 1095s, 1028w, 999w, 742s, 693vs,

544m, 522vs; ^{1}H NMR(300 MHz, CD_2Cl_2, -30°C) δ 7.5-7.8(aromatics,12H), 7.3-7.4 (aromatics, 18H), 5.7-6.1(m, 4H), 5.12(br, 1H), 3.16(br, 1H), 0.95(br, 1H); ^{13}C NMR(75MHz, CD_2Cl_2, -30°C) δ39.8, 120.3, 123.5, 124.6, 127-136(multiple peaks),144.2; ^{31}P NMR(121 MHz, CD_2Cl_2, -30°C) δ16.3 (td, $^{1}J_{Pt-P}$=1569 Hz, $^{2}J_{P-P}$=14.6 Hz), 15.8(td, $^{1}J_{Pt-P}$=4580 Hz, $^{2}J_{P-P}$=14.6 Hz), ^{195}Pt NMR(64MHz, CD_2Cl_2, -30°C) δ -4538.7(dd, $^{1}J_{Pt-P_1}$=1570 Hz, $^{1}J_{Pt-P_2}$=4598 Hz). Anal. calcd. for $C_{43}H_{37}P_2Pt$: C, 57.99; H, 4.17. Found: C, 57.48; H, 4.19.

Preparation of *trans*-(Bromo)(1-η^1-cycloheptatrienylidene)bis (triphenylphoshine)platinum Tetrafluoroborate 1-12

Trans-(bromo)(η^1-cyclohepta-1,3,5-trienyl)bis(triphenyl-phosphine)platinum 4-9 (180 mg,0.2 mmole) was dissolved in 15 ml of methylene chloride in a Schlenk tube with a stirring bar; $Ph_3C^+BF_4^-$ (100 mg, 0.3 mmole) was also dissolved in 5 ml methylene chloride and transferred to a syringe. The $Ph_3C^+BF_4^-$ solution was then added to the Schlenk tube at room temperature. After the reaction mixture had been stirred for one hour, 30 ml hexane was added to the Schlenk tube and the product 1-12 (170 mg) precipitated out as greenish yellow solid. Yield: 87 %. The product was purified by recrystallization from CH_2Cl_2/hexane. Mp 263°C dec; IR 1586w,1481m, 1456s, 1435s, 1310w, 1187w, 1056s, 998m, 745m, 693s, 618w, 593w, 526s, 499m; FAB MS m/e: 889 (M^+), 890 (MH^+); ^{1}H NMR (300MHz, CD_2Cl_2, δ) 8.89 (d, H_α, $^{3}J_{Pt-H}$=64.0 Hz, $^{3}J_{H-H}$=11.7 Hz), 7.42 (m, H_β), 8.09 (m, H_γ), 7.53 (m, Ph),

7.25-7.45 (m, Ph); ^{13}C NMR (75MHz, CD_2Cl_2, δ) 210.5 (d, C_{carb}, $^1J_{Pt-C}$=969.0 Hz, $^2J_{P-C}$=6.5 Hz),162.5(s, C_α, $^2J_{Pt-C}$=21.2 Hz), 143.5 (s, C_β, $^3J_{Pt-C}$=90.0 Hz), 146.5 (s, C_γ); 128.4 (t, C_{ipso} of Ph, $^2J_{Pt-C}$=30.0 Hz, $^1J_{P-C}$=30.0 Hz), 135.0 (t, C_{ortho} of Ph, $^2J_{P-C}$=5.9 Hz), 129.0 (t, C_{meta} of Ph, $^3J_{P-C}$=5.1 Hz), and 131.8 (s, C_{para} of Ph); ^{31}P NMR (121MHz, CD_2Cl_2, δ) 20.7 ($^1J_{Pt-P}$=2777.4 Hz); ^{195}Pt NMR (64MHz, CD_2Cl_2, δ) -4095. Anal. calcd. for $C_{43}H_{36}PtBrP_2BF_4$: C, 52.87; H, 3.69. Found: C, 52.84; H, 3.81;

Preparation of (1,2-η²-Cyclohepta-3,5-dien-1-yne)bis(triphenylphoshine)platinum 1-13 and (1,2-η²-Cyclohepta-3,6-dien-1-yne)bis(triphenylphoshine)platinum 1-14

Tris(triphenylphosphine) platinum (0.5g, 0.5 mmole) and LDA (0.15g, 1.4 mmole) were dissolved in 12 ml of THF. To this solution was added dropwise at -10°C 0.15g (0.88 mmole) of the mixture of 2-1, 2-2 and 2-3 in 2 ml of THF . The solution was then warmed to room temperature and filtered through silica gel. Hexane (40 ml) was added to the filtrate. Any resulting precipitate was removed by filtration through silica gel again. The products (0.17g) were collected as a mixture of yellow crystals of 1-13 and 1-14 by slow evaporation of the solvents. Yield: 43 %. Mp 174°C dec.; IR 3051w, 3006w, 2810w, 1963w, 1712m, 1478s, 1433s, 1307w, 1182m, 1094s, 1026m, 998m, 860w, 744s, 696s, 678m, 543s, 522s, 510s, 500s, 426m; MS m/e: 809 (M^+); 1-13 and 1-14 cannot be separated, but with the help of various NMR

techniques, their NMR resonances can be clearly assigned except in the phenyl region (which is 7.0-8.0ppm in ^{1}H NMR and 128, 129, 134 and 138ppm in ^{13}C NMR). For 1-13 ^{1}H NMR (300MHz, CD_2Cl_2, δ) 3.32 (d, H7, $^{3}J_{Pt-H}$=30.2 Hz, $^{3}J_{H-H}$=4.7 Hz), 5.22 (m, H6), 5.75 (m, H5), 5.77 (m, H4), 5.88 (d, H3, $^{3}J_{Pt-H}$=40.3 Hz, $^{3}J_{H-H}$=8.8 Hz); ^{13}C NMR (75MHz, CD_2Cl_2, δ) 28.9 (C7), 125.1 (C6), 127.8 (C5), 126.8 (C4), 121.2 (C3); ^{31}P NMR (121MHz, CD_2Cl_2, δ) 28.0 (for both of the P nuclei, but their coupling constants to the Pt are different: $^{1}J_{Pt-P1}$=3370.2 Hz, $^{1}J_{Pt-P2}$=3404.4 Hz); ^{195}Pt NMR (64MHz, CD_2Cl_2, δ) -4667. For 1-14: ^{1}H NMR (300MHz, CD_2Cl_2, δ) 6.38 (d, H_α, $^{3}J_{Pt-H}$=33.0 Hz, $^{3}J_{H-H}$=8.8 Hz), 5.10 (m, H_β), 2.42 (t, H_γ, $^{3}J_{H-H}$=7.0 Hz); ^{13}C NMR (75MHz, CD_2Cl_2, δ) 123.2 (C_α), 114.2 (C_β), 30.0 (C_γ); ^{31}P NMR (121MHz, CD_2Cl_2, δ) 27.2 ($^{1}J_{Pt-P}$=3392.4 Hz); ^{195}Pt NMR (64MHz, CD_2Cl_2, δ) -4689. Anal. calcd. for $C_{43}H_{36}PtP_2$: C, 63.78; H, 4.48. Found: C, 63.76; H, 4.55.

Preparation of (Tropyne)bis(triphenylphoshine)platinum 1-15

The mixture of (1,2-η^2-cyclohepta-3,5-dien-1-yne)bis(triphenylphoshine)platinum 1-13 and (1,2-η^2-cyclohepta-3,6-dien-1-yne)bis(triphenylphoshine)platinum 1-14 (81 mg, 0.1 mmole) was dissolved in 1 ml of methylene chloride in a Schlenk tube with a magnetic stirring bar. $Ph_3C^+BF_4^-$ (34 mg,0.1 mmole) was also dissolved in 1 ml methylene chloride and transferred to a syringe. The Schlenk tube was cooled to -78°C and the $Ph_3C^+BF_4^-$ solution was added slowly. The yellow solution changed to red after adding a few

drops of the $Ph_3C^+BF_4^-$ solution. After all the $Ph_3C^+BF_4^-$ solution had been added, about 25 ml of ethyl ether was added to the solution and and the Schlenk tube was warmed to room temperature. A red precipitate was formed. The product 1-15 (76 mg) was obtained by filtering the solution and drying the precipitate on a vacuum line. Yield: 85 %. Mp 137°C, dec; IR 3054w, 2358m, 2337m, 1634m, 1435s, 1418s, 1098s, 1058s 998m, 957m, 744m, 695s, 524s, 510s, 497m; ^1H NMR (300MHz, CD_2Cl_2, δ) 7.66 (m, H2, $^3J_{Pt-H}$=51.9 Hz), 8.34 (m, H3), 8.64 (t, H4, $^3J_{H-H}$=10.0 Hz), 7.20 (m, Ph), 7.40 (m, Ph); ^{13}C NMR (75MHz, CD_2Cl_2, δ) 174.6 (dd, C1 $^1J_{Pt-C}$=458.5 Hz, $^2J_{Ptrans-C}$=83.4 Hz, $^2J_{Pcis-C}$=5.0 Hz),135.6(m, C2), 150.0 (d, C3, $^3J_{Pt-C}$=53.2 Hz, $^4J_{Ptrans-C}$=10.5 Hz), 141.8 (s, C4); 133.1(d, C_{ipso} of Ph, $^2J_{Pt-C}$=324.1 Hz, $^1J_{P-C}$=50.6 Hz), 134.3 (d, C_{ortho} of Ph, $^2J_{P-C}$=13.4 Hz, $^3J_{Pt-C}$=16.2 Hz),129.1 (m, C_{meta} of Ph, $^3J_{P-C}$=10.7 Hz), and 131.4 (s, C_{para} of Ph); ^{31}P NMR (121MHz, CD_2Cl_2, δ) 21.5 ($^1J_{Pt-P}$=3121.8 Hz); ^{195}Pt NMR (64MHz, CD_2Cl_2, δ) -3788. Anal. calcd. for $C_{43}H_{35}PtP_2BF_4 \cdot 1/2\ CH_2Cl_2$: C, 55.68; H, 3.84. Found: C, 55.37; H, 3.80.

X-ray Structural Studies

For 1-9: $C_{43}H_{36}P_2Pt$, M_r = 809.82, Monoclinic, P $2_1/c$, a = 13.664(7)), b = 16.783(8), c = 16.702(8) Å, β = 111.68(4)°, V = 3559(3) $Å^3$, Z = 4, D_x = 1.51 g cm^{-3}, MoK_α (λ = 0.71069 Å), μ = 41.00 cm-1, F(000) = 1608, T = 298 K, R = 0.0329 and wR = 0.0366 for 3807 reflections [$I \geq 3\sigma$ (I)].

For 1-13: $C_{43}H_{36}P_2Pt$, M_r = 809.7, Monoclinic, $P2_1/c$, a = 13.544(2) Å, b = 17.235(3) Å, c = 16.163(2) Å, β = 107.93(1)°, V = 3590(1) Å^3, Z = 4, $D_{calc.}$ = 1.498 g cm^{-3}, Mo Kα (λ = 0.71069 Å), T = 298 K, R = 0.0449 and wR = 0.0456 for 2811 reflections [$I \geq 3\sigma(I)$].

For 1-15: $C_{43}H_{35}P_2Pt^+ BF_4^-$. 1/2 CH_2Cl_2, M_r = 938.0, Orthorhombic, Pbca, a = 16.615(2) Å, b = 15.709(4) Å, c = 30.263(3) Å, V = 7899(2) Å^3, Z = 8, $D_{calc.}$ = 1.578 g cm^{-3}, Mo Kα (λ = 0.71069 Å), T = 298 K, R = 0.0441 and wR = 0.0423 for 2734 reflections [$I \geq 2\sigma(I)$].

All data were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing MoKα radiation (λ = 0.71069 Å). For 1-9, 25; for 1-13 and 1-15, 40 reflections with $20.0° \leq 2\theta \leq 22.0°$ were used to refine the cell parameters. For 1-9, 5540; for 1-13, 5091; and for 1-15, 5587 reflections were collected using the ω-scan method. Four reflections (102; $\bar{1}\bar{6}6$; $\bar{2}\bar{1}0$; 060 for 1-9), (040, $\bar{1}\bar{1}3$, $0\bar{3}\bar{1}$ for 1-13) and (042, $13\bar{1}$, $32\bar{3}$, $0\bar{4}0$ 1-15) were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was<1.03 % for 1-9, was<1.02 % for 1-13 and was < 1.04 % for 1-15). Absorption corrections were applied based on measured crystal faces using *SHELXTL plus* (Sheldrick, 1990); absorption coefficient, μ = 40.3 cm^{-1} for 1-13 and μ = 37.4 cm^{-1} for 1-15; minimum and maximum transmission of 0.561 and 0.674 for 1-13, 0.534 and 0.680 for 1-15, respectively.

The structure of 1-9 was solved by the heavy-atom method (Patterson in *SHELXTL*) from which the position of the Pt atom was obtained. The positions of the rest of the non-H atoms were obtained from a subsequent Difference Fourier map. The structure was refined [*SHELX76* [89]] using cascade-matrix least squares. All phenyl H-atoms were calculated in idealized positions; each was given a fixed isotropic thermal parameter equal to 1.2 times the equivalent isotropic thermal parameter of the C-atom to which it is bonded. The allene H-atoms were obtained from a Difference Fourier map and refined with no constraints; H(6) was calculated in an idealized position but its thermal parameter was allowed to refine. All non-H atoms were refined with anisotropic thermal parameters. A total of 436 parameters were refined and $\sum w (|F_o| - |F_c|)^2$ was minimized; $w=1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5\ kI^{-1/2}\ \{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, I(intensity)= ($I_{peak} - I_{background}$)(scan rate), and $\sigma(I) = (I_{peak} + I_{background})^{1/2}$ (scan rate), k is the correction due to decay and Lp effects, 0.02 is a factor used to downweight intense reflections and to account for instrument instability. Final R = 0.0329, wR = 0.0366 (R_{all} = 0.0613, wR_{all} = 0.0449) for 3807 reflections having $I \geq 3\sigma(I)$, and goodness-of-fit =1.22 . Maximum Δ/σ = 0.02 in the final refinement cycle and the minimum and maximum peaks in the ΔF map were -0.91 and 1.47 e $Å^{-3}$, respectively. The highest peak in ΔF map is 1.11 Å from the Pt atom and thus was attributed to its anisotropy. The linear absorption coefficient was calculated using values from the

International Tables for X-ray Crystallography (1974)[90]. Scattering factors for non-hydrogen atoms were taken from Cromer & Mann (1968)[91] with anomalous-dispersion corrections from Cromer & Liberman (1970),[92] while those of hydrogen atoms were from Stewart, Davidson & Simpson (1965).[93] The thermal ellipsoids drawing (*SHELXTL*, Sheldrick, 1986)[94] of the molecule with the atom labelling scheme is given in Fig.2-8.

The structures of 1-13 and 1-15 were solved by the heavy-atom method in *SHELXTL plus* (Scheldrick, 1990)[95] from which the location of the Pt atoms were obtained. The rest of the non-hydrogen atoms were obtained from a subsequent difference Fourier map. The structures of 1-13 and 1-15 were refined in *SHELXTL plus* using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the positions of the hydrogen atoms were calculated in ideal positions and their isotropic thermal parameters were fixed. 415 (for 1-13) and 489 (for 1-15) parameters were refined, respectively, and $\sum w (|F_o| - |F_c|)^2$ was minimized; $w=1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5\ kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2 \}^{1/2}$, I(intensity)= ($I_{peak} - I_{background}$)(scan rate), and $\sigma(I) = (I_{peak} + I_{background})^{1/2}$ (scan rate), k is the correction due to decay and Lp effects, 0.02 is a factor used to down weight intense reflections and to account for instrument instability. The linear absorption coefficient was calculated from values from the *International Tables for X-ray Crystallography* (1974).[90] Scattering factors for non-hydrogen atoms were taken from Cromer & Mann (1968)[91] with anomalous-

dispersion corrections from Cromer & Liberman (1970),[92] while those of hydrogen atoms were from Stewart, Davidson & Simpson (1965).[93]

CHAPTER 10
SUMMARY

The proton NMR spectrum of 1-9 was characterized by deuterium labeling, NMR COSY and NOE. From an X-ray crystal structural study of 1-9, it was found that the dihedral angle between H3 and H2 in 1-9 is nearly 90°. This result explains why there is no coupling between H3 and H2, a fact which had caused the COSY spectrum to be misleading.

The fluxional process of 1-9 was studied by NMR spin saturation transfer and NOESY. The activation parameters were determined: $\Delta H^{\neq}$=26.8 Kcal/mole, $\Delta S^{\neq}$=15.1 eu. The mechanism of the fluxional process was found to be intermolecular. The fluxional process of 5-1 was found to be significantly slower than that of 1-9.

The first tropyne complex 1-15 and the first (*trans*-bromobistriphenylphosphine)(cycloheptatrienylidene) platinum complex 1-12 were prepared. Their structures were characterized by standard identification methods (NMR, IR, etc.). The NMR data of these two complexes are discussed in terms of σ-bonding and π-back bonding interaction between the metal fragments and the tropylium ion ligand. The successful preparation of 1-12 also provides more evidence to support the suggestion that the seven-membered ring form of C_7H_6 prefers a cycloheptatetraene (allene) form to a cycloheptatrienylidene (carbene) form if it is complexed to a

high-electron-density metal fragment, e.x., Pt(0), which has ten d electrons, but this preference will be reversed if C_7H_6 is complexed to a low electron density metal such as Pt(II) which has eight d electrons.

The mechanisms of the formation of 5-1 and 1-9 were investigated. The possibility of the so-called insertion mechanism was excluded, but both a trapping mechanism and a π-complex mechanism remain viable possibilities.

Finally, lithium diisopropylamide (LDA) was discovered to be a good base for removing HBr from a double bond in cyclic alkene compounds, and for producing cyclic alkyne complexes of bistriphenylphosphineplatinum. Using this base, complexes of cycloheptyne, cyclohexyne, cyclohepta-3,5-dien-1-yne and cyclohepta-3,6-dien-1-yne were successfully prepared.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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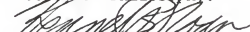

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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